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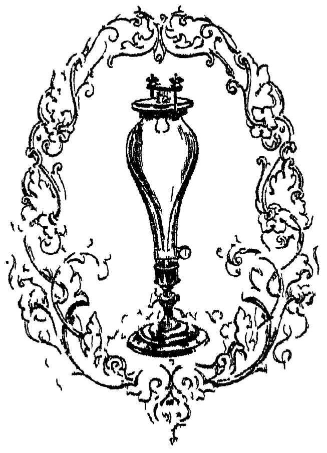

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HAND-BOOK

OF

CHEMISTRY.

BY

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MARBURG, MUNICH, PARIS, PETERSBURGH, VIENNA, AND WETTERAU.

VOL. IV.

METALS—*(continued.)*

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METALS,

(*Continued.*)

CHAPTER XVII.

TANTALUM.

Hatchett. *Crell. Ann.* 1802, 1, 197; also *Scher. J.* 9, 363; also *Gilb.* 11, 120.—Further: *Crell. Ann.* 1802, 1, 257 & 352.
Ekeberg. *Schr. J.* 9, 597; also *Crell. Ann.* 1803, 1.
Wollaston. *Schw.* 1, 520; also *Gilb.* 37, 98.
Gahn, Berzelius & Eggertz. *Schw.* 16, 437.
Berzelius. *Pogg.* 4, 6.
Wöhler. *Pogg.* 48, 91; also *Ann. Pharm.* 31, 120.
H. Rose. *Pogg.* 63, 307 and 693; 69, 118; also *N. Ann. Chim. Phys.* 13, and 350; 19, 165.

SYNONYMES: *Columbium, Tantale, Tantal.*

History.—Discovered by Hatchett, in 1801, as *Columbium*, in an American mineral, and by Ekeberg in 1802 as *Tantalum*, in two Swedish minerals. Wollaston, in 1809, pointed out the identity of these two metals. Berzelius, in 1824, prepared pure metallic tantalum and many of its compounds previously unknown. ¶ In 1846, H. Rose discovered that the metal hitherto called *tantalum* and regarded as a simple substance, is really a mixture of at least two different metals, and in some cases probably of three. The name of tantalum is retained for one of the three allied metals, and the other two have received the names of *Niobium* and *Pelopium.* The following details, therefore, excepting where otherwise expressly indicated, must be understood to refer to tantalum as it was understood previous to Rose's investigations. ¶

Sources.—As tantalic acid (rarely tantalous acid) in combination with various salifiable bases in Tantalite, Yttro-tantalite, Euxenite, Fergusonite, Pyrochlore, and Urano-tantalite. (*Vid.* Niobium and Pelopium, p. 15.)

Preparation and *Properties.*—1. Anhydrous fluoride of tantalum and potassium is heated with potassium, and the fluoride of potassium, which is produced with incandescence, dissolved out by water.—Black, heavy powder, which becomes iron-grey under the burnishing steel; it does not conduct electricity, or at least with great difficulty, probably in consequence of its pulverulent state. Very refractory in the fire. (Berzelius.)

2. When tantalic acid is heated in a charcoal crucible in a blast-furnace, tantalous acid is formed, surrounded with a thin, yellowish stratum of reduced tantalum, having a faint metallic lustre; this stratum conducts electricity very well, and when polished with agate, acquires a high metallic lustre and a more decided iron-grey colour. (Berzelius, *Lehrbuch.*)

3. Children (*Schw.* 16, 365), by exposing tantalic acid to the influence of his powerful voltaic battery, obtained very brittle granules of a reddish yellow colour.

¶ 4. By passing dry ammoniacal gas over chloride of tantalum ignited in a tube. (Rose, *Pogg.* 69, 115.)

The tantalum prepared by the first and fourth methods takes fire in the air at a lower temperature than that obtained by the second. (Berzelius.) ¶

Compounds of Tantalum.

Tantalum and Oxygen.

A. Tantalous Acid. TaO^2.

Oxide of Tantalum.—Occurs in the form of tantalite of protoxide of iron, in the Tantalite of Kimito.

Preparation.—Ignited tantalic acid is pressed into a cavity not larger than a quill, made in the middle of a charcoal crucible, and ignited for an hour in the strongest heat of a blast-furnace. A trace of metallic tantalum is produced on the surface only.

Properties.—Unfused, porous, dark grey mass, having the form of the bore, only more contracted. When rubbed on the whetstone, it acquires a metallic steel-grey colour. It scratches glass and yields a dark brown powder, destitute of metallic lustre; it is a non-conductor of electricity. (Gahn, Berzelius & Eggertz.) Ekeberg, by exposing oxide of tantalum to a white heat in a charcoal crucible, obtained a moderately hard, blackish grey mass, having somewhat of the metallic lustre; Hatchett obtained a black powder.

			Berzelius.
Ta	185	92·04	92·02
2O	16	7·96	7·98
TaO^2	201	100·00	100·00

(TaO = 1153·72 + 100 = 1253·72. Berzelius.)

Tantalous acid is not reduced when treated with zinc and aqueous hydrochloric acid, after ignition; that which contains sulphuric acid and has been previously dried, becomes blue, without being dissolved; but if moist it dissolves, yielding first a fine blue and afterwards a dark brown solution (hydrochlorate of tantalous acid?). Ammonia added to this solution precipitates dark brown flakes (of hydrated tantalous acid?), which again become white on exposure to the air. (Wöhler.)

B. TANTALIC ACID. TaO^3.

Oxide of Tantalum, Tantaloxyd, Tantalerde, Acide Tantalique, Oxyde de Tantale.

Formation.—1. Tantalum prepared by the first method, takes fire in the air at a temperature considerably below redness, and burns with great splendour, yielding pure tantalic acid. When fused with hydrate or carbonate of potash, it decomposes the water or carbonic acid and forms tantalate of potash. It dissolves in aqueous hydrofluoric acid, with rise of temperature and evolution of hydrogen gas; and very rapidly in a mixture of hydrofluoric and nitric acids. Nitric acid, after long boiling, dissolves only a trace; boiling oil of vitriol behaves in a similar manner, and its action is increased by the addition of nitric acid. Hydrochloric acid or nitric acid alone, and solution of caustic potash, have no action on the metal. (Berzelius.)

2. Tantalous acid does not absorb oxygen in the air at ordinary temperatures; the peculiar odour which it evolves in a moist atmosphere, arises from the presence of a small quantity of manganese. When heated to redness it becomes incandescent and remains so, provided the temperature be kept up, till the whole is converted into greyish white tantalic acid; during this process, it absorbs from 3·5 to 4·2 per cent. of oxygen. Ignited with potash or nitre, it yields tantalate of potash; in the latter case a slight explosion occurs. It is not affected by hydrochloric acid, aqua-regia, hydrofluoric acid, or a mixture of hydrofluoric and nitric acids. (Gahn, Berzelius & Eggertz.)

Preparation.—1. Levigated tantalite is fused with 2 parts of hydrate of potash; the resulting mass dissolved in hot water; and the filtered solution supersaturated with hydrochloric or nitric acid; the hydrated tantalic acid is then precipitated (though not entirely: *Berzelius*) in white flakes, which are purified by washing with water. (Ekeberg.)—2. One part of tantalite is ignited with 5 parts of carbonate of potash and 2 parts of borax, and the fused mass digested in water and supersaturated with hydrochloric acid; hydrated tantalic acid then remains, and must be well washed with pure water. (Wollaston.)—3. A mixture of one part of finely divided tantalite and from 6 to 8 parts of bisulphate of potash is heated to redness in a platinum crucible, till the whole fuses to a perfectly clear liquid, and no undissolved matter can be observed at the bottom of the crucible. The mass, when cold, is reduced to powder, and repeatedly boiled with fresh quantities of water, till no more sulphate of potash, iron, or manganese is dissolved; the undissolved hydrate of tantalic acid containing sesquioxide of iron, binoxide of tin, and tungstic acid, is digested with bihydrosulphate of ammonia, which removes the two latter substances, and converts the ferric oxide into ferrous hydrosulphate; the liquid is then filtered; and the insoluble tantalic acid washed with water containing bihydrosulphate of ammonia. The washed residue is boiled with concentrated hydrochloric acid till its green colour is changed to white; the hydrochloric acid poured off; and the hydrated tantalic acid washed with boiling water. (Berzelius.)—The hydrate prepared by either of these processes may be converted into pure tantalic acid by ignition.—To obtain it as free as possible from silica, the hydrate must be dissolved in aqueous hydrofluoric acid; the filtered solution mixed with sulphuric acid and evaporated to dryness; and the residue ignited as long as it loses weight; the whole of the silica is then expelled in the form of gaseous fluoride of silicium. (Berzelius.)

Properties. White infusible powder; fixed in the fire, tasteless and inodorous; does not redden litmus; specific gravity = 6·5. (Ekeberg.) Assumes a lemon-yellow colour every time it is heated. (Wöhler.) ¶ The specific gravity of tantalic acid varies considerably, according to the temperature to which it has been exposed, and also according to its molecular condition. The specific gravity of the amorphous acid, prepared from the chloride and heated to the point of incandescence over a spirit-lamp, is 7·280; that of the crystallized acid [obtained by precipitation?] is = 7·284. On exposing these acids to the heat of a strong charcoal fire for four hours, the specific gravity increased to 7·851, and in one instance to 7·9944; but when they were ignited in a porcelain-furnace, the specific gravity was reduced to 7·783, the acid remaining unchanged in appearance. Specific gravity of tantalic acid obtained from the Ytterby tantalite = 7·43. The greatest and the least observed specific gravities of tantalic acid are respectively, 8·264 and 7·022.

			Berzelius.
Ta	185	88·51	88·487
3O	24	11·49	11·513
TaO^3	209	100·00	100·000

$Ta^2O^3 = 2 \;.\; 1153{\cdot}72 + 3 \;.\; 100 = 2607{\cdot}44$. (Berzelius.)

Decompositions. In the circuit of a powerful voltaic battery, tantalic acid is reduced to the metallic state. (Children.)—2. When exposed to a white heat in contact with charcoal, it is partly reduced to the metallic state, and partly to tantalous acid; by passing hydrogen gas over tantalic acid heated to redness in a tube, it is converted, though with a scarcely perceptible loss of weight, into a grey (bluish-black: *Wöhler*) oxide, which, when ignited in the air, again becomes white. (Gahn, Berzelius & Eggertz.) Probably a mixture of tantalic with tantalous acid. (Wöhler.)—3. By ignition with bisulphide of carbon, tantalic acid is converted into sulphide of tantalum, carbonic oxide, and free sulphur: $TaO^3 + 3CS^2 = TaS^3 + 3CO + 3S$.—4. Heated with hydrofluoric acid, it yields fluoride of tantalum. ¶ 5. Tantalic acid remains colourless when ignited in an atmosphere of hydrogen or hydrosulphuric acid gas, but when ignited in a current of ammoniacal gas, it turns grey and yields a small quantity of water. (Rose.) ¶

Combinations. a. With Water:—Hydrated Tantalic Acid.—Obtained by precipitating a solution of tantalate of potash in water by hydrochloric acid, and washing the precipitate with hot water, till it passes through the filter free from hydrochloric acid. Snow-white, bulky precipitate, which reddens litmus-paper when laid on it in a moist state, and becomes orange-coloured when treated with infusion of galls. (Gahn, Berzelius & Eggertz.)

	Calculation.		Gahn, Berzelius & Eggertz.		
TaO^3	209	88·56	88·83	to	89·5
3HO	27	11·44	11·17	„	10·5
$TaO^3, 3HO$	236	100·00	100·00	„	100·0

When heated in a retort, it evolves water which is neutral to test-paper, and leaves the pure acid behind (Gahn, Berzelius & Eggertz);

according to Berzelius, an emission of light is sometimes observed during this process. Becomes phosphorescent by ignition. (Rose.)

b. With Acids:—Tantalic acid, after ignition, is (according to Berzelius) insoluble in all acids, unless it has been again fused with potash or bisulphate of potash. The hydrated acid dissolves abundantly in hydrofluoric acid and acid oxalate of potash—slightly in sulphuric and hydrochloric acid—and not at all, or in very small quantity, in nitric, oxalic, tartaric, citric, acetic, or succinic acid, or in cream of tartar. (Gahn, Berzelius & Eggertz.) These solutions are colourless; some of them yield a precipitate on the addition of water; others form a white opaque jelly with concentrated aqueous solution of phosphoric acid. Alkaline carbonates and hydrosulphates disengage carbonic acid or sulphuretted hydrogen, and throw down white flakes of hydrated tantalic acid. Ferrocyanide of potassium communicates a yellow colour to a solution of tantalic acid in acid oxalate of potash. Infusion of galls, provided the solution does not contain too large an excess of acid, produces an orange colour, and when added in larger quantity, a precipitate of the same colour. ¶ This precipitate is not produced in the presence of non-volatile organic acids, and is moreover redissolved by caustic alkalis. (Rose.) ¶ Zinc gives a white precipitate.

c. With Salifiable Bases, forming the TANTALATES. Tantalic acid has a greater affinity for bases, and especially for the fixed alkalis, than for acids. It yields with them soluble and insoluble compounds, both in the wet and in the dry way. The stronger acids throw down hydrated tantalic acid from solutions of its salts, in the form of a milk-white precipitate which is characterized by its insolubility in acids and by not imparting a colour to fluxes before the blowpipe. Tincture of galls throws down an orange-coloured precipitate from an alkaline (acid, *Rose*) solution of tantalic acid, provided the alkali is not in very great excess. Hydrosulphate of potash and ferrocyanide of potassium do not produce any precipitate.

¶ Alkaline tantalates are completely precipitated by chloride of ammonium and sulphate of ammonia at ordinary temperatures. The precipitate is an acid salt, containing both fixed alkali and ammonia. The precipitate produced in alkaline tantalates by hydrochloric acid, redissolves in an excess of the acid, forming an opalescent solution which is but partially precipitated by sulphuric acid, even on boiling. The alkaline salts are decomposed by a current of carbonic acid; hence a neutral solution of tantalate of soda becomes turbid on exposure to the air. Tantalate of soda acidulated with sulphuric acid yields a yellow flocculent precipitate with ferrocyanide of potassium, and a white precipitate with the ferricyanide: the former is slightly soluble in a large quantity of hydrochloric acid. When a solution of tantalate of soda is mixed with an acid, and a piece of zinc is plunged into it, a white precipitate of tantalic acid is formed after some time. The insolubility of tantalate of soda in excess of caustic soda or carbonate of soda, and consequently the fact that a strong solution of this salt is precipitated on the addition of either of these reagents, is a character which distinguishes this acid from all others (excepting niobic and pelopic acid), more especially from tungstic acid, which it otherwise much resembles. (Rose.) ¶

TANTALUM AND BORON.

BORATE OF TANTALIC ACID.—Tantalic acid dissolves in melted boracic acid, yielding a colourless glass. (Ekeberg.)

TANTALUM AND PHOSPHORUS.

Phosphide of Tantalum has not yet been prepared.

PHOSPHATE OF TANTALIC ACID.—*a.* Tantalic acid fuses with phosphoric acid, forming a colourless glass (blue, when tungstic acid is present). (Ekeberg.)

b. A concentrated aqueous solution of phosphoric acid added to a solution of tantalic acid in sulphuric or hydrochloric acid, causes the separation of a white, opaque jelly. (Thénard.)

TANTALUM AND SULPHUR.

A. SULPHIDE OF TANTALUM.—1. Tantalum heated in sulphur-vapour takes fire at a temperature approaching redness, and burns with great rapidity, forming sulphide of tantalum. (Berzelius.)—2. Vapour of bisulphide of carbon is passed over tantalic acid at a white heat—as in the preparation of sulphide of titanium (p. 477). (H. Rose, *Gilb.* 73, 139.) No sulphide of tantalum is produced by igniting tantalum with sulphur; or by igniting tantalic acid with sulphur or cinnabar, or in a current of hydrosulphuric acid gas. (Gahn, Berzelius & Eggertz.) Tantalic acid is not decomposed, either in the dry or wet way, by sulphide of potassium. (Berzelius.)

Grey, smooth, fine-grained mass, which can be compressed into steel-grey lumps, having a metallic lustre, resembling graphite in appearance, and conducting electricity. (Rose, Berzelius.)

		According to Berzelius.
Ta	185	79·40
3S	48	20·60
TaS^3	233	100·00

Sulphide of tantalum, when heated in the air to incipient redness, burns with a bluish, sulphurous flame, and is converted into tantalic acid, the sulphur being driven out and replaced by oxygen. A portion of sulphuric acid, however, is so strongly retained by the tantalic acid, that it can scarcely be got rid of, except by ignition with carbonate of ammonia. 100 parts of sulphide of tantalum yield from 89·6 to 89·743 parts of tantalic acid. Sulphide of tantalum fused with hydrate of potash in a close vessel, dissolves, and forms a yellowish red mixture of tantalate of potash with double sulphide of tantalum and potassium, translucent and greenish blue at the edges. On the addition of water, this substance immediately becomes black, in consequence of the reproduction of sulphide of tantalum, the whole of the potash being dissolved in the free state by the water. The sulphide of tantalum [hydrated?] thus precipitated, is a black powder, which appears dark greenish blue by transmitted light. When not protected from the air, it oxidizes in a few hours, and is converted into white tantalic acid. When chlorine gas is passed over sulphide of tantalum at ordinary temperatures, the sulphide becomes heated in the course of two hours, and is converted, without incandescence, into chloride of tantalum and chloride of sulphur. The decomposition is facilitated by heat. A mixture of hydrofluoric and nitric acids dissolves sulphide of tantalum, leaving a residue of sulphur; boiling aqua-regia converts it into sulphuric acid and tantalic acid, the latter of which remains almost wholly undissolved. Sulphuric acid, hydrochloric acid, hydrofluoric acid, nitric acid, and caustic potash, have no action on sulphide of tantalum. (Berzelius.)

B. SULPHATE OF TANTALIC ACID.—*a. Basic Sulphate.*—Water added to the solution *b*, precipitates tantalic acid, which obstinately retains a portion of the sulphuric acid, and parts with it only on ignition—more readily however on the addition of carbonate of ammonia. The same compound remains when sulphide of tantalum is burned. (Berzelius.) It likewise separates from a fused mixture of tantalic acid and bisulphate of potash on the addition of water. It is soluble, while moist, in hydrochloric acid and solution of potash. (Wöhler.)

b. Acid Sulphate.—Hydrated tantalic acid dissolves sparingly in oil of vitriol. From this solution water precipitates the compound *a*.

TANTALUM AND CHLORINE.

A. CHLORIDE OF TANTALUM.—$TaCl^3$.—Tantalum heated in chlorine gas burns with great rapidity, producing a dark yellow vapour which condenses to a yellowish white, amorphous powder. This compound is also obtained by gently heating the mixture of chloride of sulphur and chloride of titanium—formed by the action of chlorine on sulphide of tantalum (see above)—till the chloride of sulphur is volatilized. Chloride of tantalum is resolved by water, with violent hissing and evolution of heat, into insoluble, translucent tantalic acid and aqueous hydrochloric acid, which retains but a small portion of tantalic acid in solution. (Berzelius.) ¶ Volatilizes at 144°; fuses at 221°. Treated with concentrated sulphuric acid at ordinary or at slightly elevated temperatures, it dissolves and forms an opalescent solution, which, when boiled, becomes very turbid, and on cooling, yields a white opalescent jelly, insoluble in acidulated water. Dissolves in hydrochloric acid at ordinary temperatures, yielding a cloudy solution, which, after some time, forms a tolerably firm jelly. On treating this substance with water, traces of tantalic acid dissolve, and are not thrown down by boiling. Boiling hydrochloric acid does not dissolve it completely, but the solution does not gelatinize on cooling; if water be now added, an opalescent solution is formed, which may be boiled without further change; sulphuric acid, even at ordinary temperatures, produces after some time a voluminous precipitate. Chloride of tantalum is not completely decomposed by boiling water; but water containing a small quantity of ammonia decomposes it perfectly at ordinary temperatures, the acid separating in flakes which are readily collected on a filter. Solution of potash does not dissolve it completely; solution of carbonate of potash leaves it untouched, even on boiling. It does not blacken when exposed to a current of hydrosulphuric acid gas at ordinary temperatures, but when heated in the gas, it evolves hydrochloric acid and is converted into sulphide of tantalum. (Rose.) ¶

B. TANTALATE OF TERCHLORIDE OF TANTALUM?—When dry chlorine gas is passed over an ignited mixture of tantalic acid and charcoal, a white sublimate is obtained, which fumes slightly in the air, and is converted by heat into a colourless vapour which condenses to a concentric, fibrous, silky mass. Sometimes the sublimate fuses partially on the application of heat, in which case it yields a yellow vapour, as though it contained an excess of chloride of tantalum: this is probably caused by the use of a larger quantity of charcoal. The compound is decomposed by water with disengagement of heat and separation of gelatinous tantalic acid containing hydrochloric acid; with hydrochloric acid, on the contrary, it forms a clear solution. (Wöhler.)

C. HYDROCHLORATE OF TANTALIC ACID.—1. Prepared by boiling hydrated tantalic acid with aqueous hydrochloric acid.—2. By mixing chloride of tantalum with water.—3. By dissolving B in hydrochloric acid. The solution is not rendered cloudy by water. On evaporation, it deposits the tantalic acid in the translucent state. The solution obtained by the third method is not clouded by boiling, except when concentrated; and in that case it again becomes clear on the addition of water; sulphuric acid, even at ordinary temperatures, precipitates nearly all the tantalic acid. (Wöhler.)

The tantalic acid containing sulphuric acid (*p.* 7, B, *a.*) dissolves with tolerable facility in concentrated hydrochloric acid, and in large quantity after long digestion. This solution, when diluted with water, becomes turbid on boiling, and gives a white precipitate of tantalic acid containing sulphuric acid. By sulphuric acid also and its salts, the tantalic acid is almost wholly precipitated from the solution, in combination with a small quantity of sulphuric acid, in the form of a heavy, milk-white precipitate: the precipitation is immediate if the liquid is hot or concentrated; gradual when it is cold and dilute. (Wöhler.)

Whereas pure chloride of tantalum is decomposed by water, depositing the greater part of the tantalic acid, chloride of tantalum mixed with chloride of sulphur (as it is obtained in the decomposition of sulphide of tantalum by chlorine) dissolves completely in water, with the exception of a small quantity of sulphur which is set free. The solution is, however, rendered turbid by heat, and deposits gelatinous tantalic acid on evaporation. (Berzelius.) [The sulphuric acid produced from the chloride of sulphur, is probably the cause of this difference of behaviour in the chlorine compound.]

TANTALUM AND FLUORINE.

A. FLUORIDE OF TANTALUM.—Formed by evaporating acid hydrofluate of tantalic acid to dryness. White, opaque, amorphous mass, which is neither volatilized nor decomposed at a red heat. By water, it is resolved into acid hydrofluate of tantalic acid which dissolves, and insoluble tantalic acid which retains a portion of hydrofluoric acid. It unites with other metallic fluorides, forming TANTALO-FLUORIDES, which are permanent in the fire, but when treated with hot water, have a tendency to be resolved into a white, insoluble powder containing excess of tantalic acid, and a solution containing a larger proportion of acid. (Berzelius.)

B. BASIC HYDROFLUATE OF TANTALIC ACID.—*a.* Ignited tantalic acid is disintegrated by aqueous hydrofluoric acid, but not dissolved; it likewise absorbs a portion of the hydrofluoric acid, which it evolves again on ignition. (Berzelius.) *b.* The precipitate produced by the action of water on fluoride of tantalum.

C. ACID HYDROFLUATE OF TANTALIC ACID.—*Hydrofluotantalic Acid.* It appears to be as yet undecided whether this compound is *tetra-hydrofluate of tantalic acid* = $TaO^3, 4HF$, (or supposing $3HO$ to be separated, = TaF^3, HF); or whether it is *penta-hydrofluate of tantalic acid* = $TaO^3, 5HF$ (or, subtracting $3HO$, = $TaF^3, 2HF$). Hydrated tantalic acid, prepared according to the third method (p. 3), dissolves instantly in aqueous hydrofluoric acid. Any tantalite which may have remained undecomposed, or any portion of tantalic acid, which, though it has given up its protoxide of iron to the bisulphate of potash, has not itself been dissolved—is left behind. The clear solution, evaporated spontaneously at first, and afterwards at a temperature of 30°, deposits crystals of acid hydrofluate of tantalic acid, together with fluoride of tantalum formed on the edge of the basin by the volatilization of the excess of hydrofluoric acid. The crystals, by mere efflorescence in the air—whereby they lose hydrofluoric acid and water—are converted into fluoride of tantalum; this change is produced more rapidly by heat. The salt, when recently prepared, dissolves in water without decomposition. (Berzelius.)

TANTALUM AND NITROGEN.

A. TANTALATE OF AMMONIA.—Hydrated tantalic acid digested with ammonia, forms with a portion of that substance, an insoluble compound which does not redden litmus paper, and, when heated or exposed to the air for a long time, again evolves the ammonia. With salts of the earths or of the heavy metallic oxides, this compound yields, by an interchange of elements, a tantalate of the earth or of the metallic oxide. (Gahn, Berzelius & Eggertz.) When a potash-solution of tantalic acid containing sulphuric acid, is mixed with excess of sal-ammoniac, a precipitate of tantalate of ammonia is obtained, which, when ignited out of contact of air, leaves bluish-black tantalic acid. (Wöhler.)

B. In carbonate of ammonia, tantalic acid is but very sparingly soluble. (Berzelius, *Lehrbuch.*)

C. FLUORIDE OF TANTALUM WITH HYDROFLUATE OF AMMONIA, or FLUORIDE OF TANTALUM AND AMMONIUM.—According to Berzelius, this compound consists of NH^4F, TaF^3. Acid hydrofluate of tantalic acid is mixed with ammonia till a permanent precipitate begins to appear, and the mixture is then evaporated to a small bulk. Scaly crystals. This compound, when heated in a platinum vessel, evolves a sublimate of hydrofluate of ammonia, together with a trace of fluoride of tantalum; while the residue consists of pure fluoride of tantalum. With water it readily forms an acid solution and deposits a white powder; the liquid on being boiled, deposits an additional quantity of powder. (Berzelius.)

TANTALUM AND POTASSIUM.

A. TANTALATE OF POTASH.—Tantalic acid fuses with hydrate of potash; it likewise expels carbonic acid—by fusion, but not in the wet way—from carbonate of potash. (Berzelius.) If the mass is allowed to cool before the decomposition is complete, the solidified crust is broken by the carbonic acid disengaged from the interior, just as in the case of titanate of potash (III., 484.) (H. Rose.) Hydrated tantalic acid is soluble in solution of caustic potash. Sulpho-tantalic acid while yet moist likewise dissolves readily and in large quantity in solution of potash. (Wöhler.) The fused compound is opaque when it contains an excess of tantalic acid; but when the potash is in excess, it has a vitreous aspect, and is perfectly soluble in pure water: it does not, however, dissolve at ordinary temperatures in water containing carbonate of potash. Accordingly when tantalic acid is fused with excess of carbonate of potash, the greater part of the undecomposed carbonate of potash may be separated by means of cold water; the residue, after being washed with cold water, is then dissolved in boiling water and evaporated out of contact of air. A non-crystalline residue remains, having a slightly metallic and unpleasant taste. From an aqueous solution of the above salt, all acids, including even the carbonic acid in the air, precipitate tantalic acid. (Berzelius.) From a solution of sulpho-tantalic acid in caustic potash, sal ammoniac precipitates the tantalic acid, though not completely, in the form of tantalate of ammonia. (Wöhler.) ¶ Tantalic acid when fused with carbonate of potash, yields a double salt of tantalate and carbonate of potash; but the solution deposits after some time, or on evaporation, a large quantity of acid tantalate of potash. Generally, when tantalic acid is fused with carbonate of potash, and the fused mass digested in water, the greater part of the acid remains undissolved in the form of acid tantalate. (Rose.) ¶

B. SULPHATE OF TANTALIC ACID AND POTASH.—Prepared by fusing tantalic acid with bisulphate of potash. The compound is decomposed by water, which leaves hydrated tantalic acid undissolved. (Berzelius.)

C. FLUORIDE OF TANTALUM AND POTASSIUM.—*a. With a smaller proportion of tantalum.* Acid hydrofluate of tantalic acid is mixed hot with potash till a precipitate begins to separate; or a solution of bihydrofluate of potash is heated with tantalic acid,—in the latter case, monohydrofluate of potash remains dissolved in the liquid. On cooling, the compound crystallizes out in anhydrous scales.

			Or:			Berzelius.
2K........	78·4	21·97	2KO	94·4	26·45	23·54
Ta........	185·0	51·83	TaO^3............	209·0	58·56	56·99
5F........	93·5	26·20	5(F—O)	53·5	14·99	*
	356·9	100·00		356·9	100·00	

[* The loss, amounting to 19·47, represents, according to Berzelius, not only hydrofluoric acid, but also a portion of silica.]

The compound is not decomposed by exposure to a white heat in platinum vessels; nor even by ignition with hydrated bisulphate of potash, from which only the excess of sulphuric acid is volatilized. With hydrated sulphuric acid, it evolves hydrofluoric acid. It is decomposed by potassium, with incandescence, yielding tantalum and fluoride of potassium. Dissolves sparingly, though without residue, in cold water, but much more readily in hot water. When boiled with water it is decomposed, a white powder being deposited, which is richer in tantalum than the portion which remains in solution.

b. With a larger proportion of tantalum.—1. Formed by adding hydrofluoric acid to a warm solution of *a*, before it begins to crystallize: the acid takes up one-third of the potash to form bihydrofluate of potash.—2. By supersaturating a solution of tantalate of potash in boiling water with hydrofluoric acid. The compound crystallizes out on cooling, in short, slender, anhydrous needles. By analysis, it is found to contain 63 per cent. of tantalic acid, and probably consists of 3 atoms of potassium, 2 atoms of tantalum, and 9 atoms of fluorine. When heated to redness, either alone or with bisulphate of potash, and also with sulphuric acid, it behaves like *a*. It is likewise difficultly soluble in water. (Berzelius.)

TANTALUM AND SODIUM.

A. TANTALATE OF SODA.—*a. Neutral salt.*—Prepared by fusing tantalic acid with hydrate or carbonate of soda. It is soluble only in hot water, the greater part again falling to the bottom as the liquid cools.—Before the blowpipe, tantalic acid expels the carbonic acid from carbonate of soda with effervescence; the resulting tantalate of soda is infusible. (Berzelius.)

¶ Transparent; becomes turbid when heated, in consequence of the separation of a white acid salt. After ignition, it is insoluble in water. It remains colourless when ignited in a current of hydrosulphuric acid gas; but all the soda is converted into double sulphide of hydrogen and sodium. If a cold solution of tantalate of soda be treated with caustic soda, and the mixture evaporated at ordinary temperatures over oil of vitriol, the resulting compound is no longer completely soluble in water.

b. Acid Salt.—1. The residue left after prolonged fusion of tantalic acid with excess of carbonate of soda and treatment of the mass with water. In this operation, the tantalic acid expels a quantity of oxygen in the carbonic acid greater than the amount contained in itself, in the proportion of 3 : 4.—2. Deposited in large quantity on boiling a solution of neutral tantalate of soda. White; it is decomposed by ignition in a current of hydrosulphuric acid gas, but remains perfectly colourless. (Rose, *Pogg.* 69, 118.) ¶

B. With borax, tantalic acid forms a colourless glass, which is rendered turbid by gentle flaming, and if it contains an excess of tantalic acid, becomes enamel-white on cooling. (Berzelius.) ¶ Rose has obtained the same results with pure tantalic acid from the Finland tantalite. ¶

C. In microcosmic salt, tantalic acid dissolves with great difficulty but in large quantity, yielding a colourless glass which remains transparent when cold. (Berzelius.) ¶ Tantalic acid yields a colourless and transparent glass in both flames: the addition of ferrous sulphate does not impart a red colour to the bead. (Rose.) ¶

D. FLUORIDE OF TANTALUM AND SODIUM.—Indistinct crystals, very soluble in water. (Berzelius.)

TANTALUM AND BARIUM.

TANTALATE OF BARYTA.—Hydrated tantalic acid digested with an aqueous solution of chloride of barium, to which a small quantity of ammonia is added, takes up at most 83·6 parts (rather more than one atom) of baryta to 209 parts (one atom) of tantalic acid, and is thereby converted into a white, insoluble powder. (Gahn, Berzelius & Eggertz.)

TANTALUM AND CALCIUM.

A. TANTALATE OF LIME.—Insoluble. (Berzelius.)

B. HYDROFLUATE OF TANTALIC ACID AND LIME.—The aqueous solution, when evaporated, gives off hydrofluoric acid and deposits a very insoluble compound, containing the same elements but in different proportions. (Berzelius.)

TANTALUM AND MAGNESIUM.

HYDROFLUATE OF TANTALIC ACID AND MAGNESIA.—The aqueous solution of this salt is likewise decomposed by evaporation, a very difficultly soluble compound being deposited. (Berzelius.)

TANTALUM AND YTTRIUM.

a. Fergusonite.—$6(YO; CeO; ThO), TaO^3$. Crystalline system, the square prismatic. Specific gravity from 5·8 to 5·86. Brownish black; translucent in thin laminæ. When heated it evolves a trace of water, becoming deep yellow at first, and subsequently pale yellow, but without fusing. Dissolves slowly in borax, forming a glass which is yellow while hot; but if saturated, is rendered turbid by flaming, and acquires a dingy yellowish red colour. The mineral dissolves slowly in microcosmic salt, yielding in the outer flame a yellow, and in the inner flame a colourless glass, which, when sufficiently saturated, assumes a reddish tint, and in that case becomes opaque on cooling or after slight flaming. It is decomposed by carbonate of soda without being dissolved, and leaves a reddish slag. (Berzelius.) It is also decomposed by fusion with bisulphate of potash.

	Atoms.			Hartwall.
CeO	1	54·0	5·98	4·68
YO	10	400·0	44·33	41·91
ZrO	1	30·4	3·37	3·02
TaO^3	2	418·0	46·32	47·75
U^2O^3				0·95
Fe^2O^3				0·34
SnO^2				1·00
	1	902·4	100·00	99·65

b. Yttro-tantalite.—*α. Brownish black variety.*—$4(CaO; YO; UO; FeO), TaO^3$.—Translucent and of a pale yellow colour, when in thin laminæ. Decrepitates slightly before the blowpipe, and assumes a light yellow colour, without fusing. With a large quantity of borax it forms a transparent, yellow glass; with a smaller quantity, a dark yellowish brown glass. It dissolves in a still larger quantity of microcosmic salt—with separation of a white skeleton, which disappears but very slowly and yields a glass which is yellow while hot and colourless when cold: if the quantity of yttro-tantalite is greater, a turbid glass is produced in the inner flame, pale green while hot, but covered with white, opaque streaks after cooling. Does not dissolve in carbonate of soda. Contains 5·7 per cent. of water. (Berzelius.)

β. Black variety.—$3(CaO; YO; FeO), (TaO^3; WO^3)$.—Specific gravity = 5·395. Scratches glass. Black; opaque; possessed of metallic lustre; decrepitates slightly before the blowpipe, and becomes dark brown, but without fusing. With borax it yields a transparent, colourless or yellowish glass, which, when it contains a comparatively small proportion of the yttro-tantalite, is rendered opaque by flaming; but when it contains a larger quantity, becomes opaque without flaming. Dissolves slowly in microcosmic salt with separation of a very insoluble skeleton, producing a colourless or yellowish glass, which, with a large quantity of yttro-tantalite in solution, becomes saffron-red and finally opaque in the inner flame. It swells up with carbonate of soda, and remains in the form of a white mass after the soda has been absorbed by the charcoal. Contains 5·4 per cent. of water. (Berzelius.) ¶ Specific gravity = 5·882 (Ekeberg); = 5·67 (Peretz); loses 5·54 per cent. of water by ignition, after which its specific gravity is 6·40. It contains pure tantalic acid free from niobic and pelopic acids. (Rose, *Pogg.* 72, 155.) ¶

γ. *Yellow variety.*—The same formula as β. Specific gravity = 5·882. (Ekeberg.) Softer than glass. Brownish yellow and opaque. Decrepitates slightly before the blowpipe, and becomes pale yellow, but does not fuse. With borax, in the inner flame, it yields a transparent, yellow glass, which becomes darker yellow on cooling, and is rendered milk-white by flaming. With microcosmic salt it behaves in a similar manner to *a*, excepting that the saturated bead assumes a fine green colour in the inner flame, and on cooling becomes pale rose-red and very turbid, owing to the presence of ferrous tungstate. Contains 4·6 per cent. of water. (Berzelius.)

All three varieties of yttro-tantalite are insoluble in aqueous acids, but are completely decomposed by fused bisulphate of potash. According to Berzelius, the water which they contain does not appear to be essential to their constitution. The following specimens were analysed after ignition:

	At.	*Yttro-tantalite, a.*		Berzelius.
CaO	11	308·0	3·18	3·26
YO	95	3800·0	39·27	38·52
UO	1	68·0	0·71	1·04
FeO	1	35·2	0·36	0·49
TaO^3	25	5225·0	54·00	51·82
WO^3	2	240·0	2·48	2·59
	1	9676·2	100·00	97·72

	At.	*Yttro-tantalite, β.*		Berzelius.
CaO	4	112·0	7·48	6·25
YO	9	360·0	24·03	20·25
UO				0·47
FeO	2	70·4	4·69	3·16
TaO^3	4	836·0	55·79	57·00
WO^3	1	120·0	8·01	8·25
	1	1498·4	100·00	95·38

Yttro-tantalite, γ; different specimens, 1 and 2.

	At.	1.		Berzelius.
CaO	2	56·0	0·57	0·50
YO	75	3000·0	30·34	29·78
UO	8	544·0	5·50	6·25
FeO	3	105·6	1·07	1·04
TaO^3	29	6061·0	61·30	60·12
WO^3	1	120·0	1·22	1·04
	1	9886·6	100·00	98·73

	At.	2.		Berzelius.		Penetz.
CaO	10	280	2·87	3·29		7·55
YO	71	2840	29·13	29·90		21·25
UO	4	272	2·79	2·99		3·94
FeO	5	176	1·81	2·44		6·29
TaO^3	29	6061	62·17	59·50		58·65
WO^3	1	120	1·23	1·25	{+ MgO and CuO}	2·40
	1	9749	100·00	99·37		100·08

The tungstic acid in α and γ 1 was found by Berzelius to contain stannic acid.—He obtained the uranium and iron in his analyses as sesquioxides, but they are calculated as protoxides.—The calculations do not quite agree with the analyses; probably from an admixture of foreign minerals.

c. *Euxenite.*—About: $4(CaO; MgO; CeO; LaO; YO; UO), 1TiO^2, 1TaO^3$, the proportion of the bases to the acids being therefore as 2 : 1.—Specific gravity = 4·60. Brownish black, with metallic, waxy lustre. Emits a faint light when heated, and gives off water. Infusible before the blowpipe. With borax, in the outer flame, it yields a brownish yellow glass, which, if a sufficient quantity of the mineral is dissolved, retains its colour on cooling, and also in the inner flame; by flaming, it is converted into a yellowish enamel. It dissolves in microcosmic salt, producing in the outer flame, a yellow glass which becomes colourless on cooling: if, however, it contains a large quantity of the mineral, it becomes green on cooling (uranium); after exposure to the inner flame, the green colour becomes darker and less pure (from admixture of the violet colour of titanium). The mineral is insoluble in hydrochloric acid and aqua-regia, but is decomposed by fusion with bisulphate of potash. It contains about 2·47 per cent. of lime, 0·29 of magnesia, 2·18 of protoxide of cerium, 0·96 of oxide of lanthanum, 25·09 of yttria, 6·34 of protoxide of uranium, 7·94 of titanic acid, 49·66 of tantalic acid, and 3·97 of water (loss 1·10). (Th. Scheerer, *Pogg.* 50, 149.)

TANTALUM AND THORINUM.

Pyrochlore:—About: $2(2[CaO; CeO; YO; ThO; MnO; FeO], TaO^3) + NaF$. Occurs in regular octohedrons, without any plane of cleavage. Sp. gr. from 4·206 to 4·326. Harder than felspar. Dark reddish brown; translucent at the edges, the transmitted light exhibiting a brown colour. When heated, it emits a faint light, and evolves water containing hydrofluoric acid. Before the blowpipe it assumes a pale, brownish-yellow colour, and fuses with great difficulty, yielding a black slag. With borax in the outer flame, it forms a clear, reddish-yellow glass, which by flaming is readily converted into a yellow enamel; or if a large quantity of the mineral is held in solution, into a white enamel. With borax in the inner flame, it forms a dark red glass, which is converted by flaming into a light greyish-blue enamel. Dissolves in microcosmic salt, with slight effervescence, yielding a glass, which, if the outer flame is used, is yellow while hot and grass-green when cold, but in the inner flame, becomes dingy green at first and then violet-red. (The pyrochlore of Fredrikswärn and Brevig behaves in this manner; that from Miask does not give the uranium reaction.) The mineral is decomposed by long digestion with oil of vitriol at high temperatures. The pyrochlore of Miask contains: lime 10·98; magnesia a trace; sesquioxide of cerium (probably protoxide in the mineral itself) with thorina 13·15; yttria 0·81; protoxide of manganese 0·15; protoxide of iron 1·29; tantalic acid 67·38; titanic and stannic acids, a trace; water 1·16 per cent. The pyrochlore of Brevig contains nearly 5 per cent. of sesquioxide of uranium and 7 per cent. of water. (Wöhler, *Pogg.* 7. 417; 48, 83.)

TANTALUM AND ALUMINUM.

TANTALATE OF ALUMINA.—Insoluble in water. (Berzelius.)

OTHER COMPOUNDS OF TANTALUM.

With *Manganese* and with *Iron.*

¶ CHAPTER XVII. (A.)

NIOBIUM.

H. Rose, *Pogg.* 63, 317; 69, 118; also *N. Ann. Chim. Phys.* 13, 350; 19, 165. Further, *Pogg.* 70, 572; 71, 157; 72, 155 and 471; 73, 455; 74, 288.

Th. Scheerer, *Pogg.* 72, 561.

History.—Wollaston (*Schw.* 6, 256; 21, 60), very soon after the discovery of tantalum, observed that the tantalite from America, and the tantalite from Finland, though to all appearance nearly the same in composition, were nevertheless of different densities. Thomson, in 1836, likewise examined a mineral containing tantalum, found at Middleton in Connecticut, and from its very low specific gravity, was induced to give it a new name, *Torrelite.* Other specimens, varying in density, were also analysed by Ekeberg & Berzelius, one of which, in consequence of the large quantity of iron which it contained, received the name of *Ferro-tantalite.* (*J. pr. Chem.* 13, 217; *Pogg.* 53.) The different densities of tantalites from different localities, and of the acid obtained from them, was likewise the first remarkable circumstance that induced Rose to enter upon a closer examination of tantalum and its compounds. Thus, it was found that black tantalite from Bodenmais has a density of 6·39, and the tantalic acid obtained from it, 6·542; reddish brown tantalite from the same locality has a density of 5·6996, the acid 5·605; tantalite of the same colour from North America, 5·708, the acid 5·452. In consequence of these facts, Rose examined more minutely into the nature of the so-called tantalic acid; and from the behaviour of the chloride, arrived at the conclusion that it contained a new metal, which he called NIOBIUM; subsequently he found in it another new metal, to which he gave the name of PELOPIUM.

Sources.—In conjunction with tantalum, in the various minerals which contain that metal; but more especially in the tantalite from Bodenmais in Bavaria, which contains niobic acid with a considerable quantity of pelopic acid; the tantalite from Massachussets, North America, which chiefly contains niobic acid; and the tantalite from the Ilmengebirg in Siberia, which contains niobic acid with mere traces of pelopic acid. Scheerer has lately found niobic acid in Pyrochlore, and variable quantities of the two acids in Eukolite or Wöhlerite, a mineral containing silica and zirconia; in Euxenite; and in a variety of Pitchblende, found in the valley of Satersdälen.

Preparation.—Niobium is reduced to the metallic state by passing a current of dry ammoniacal gas over the chloride. The reduction is attended with rise of temperature and evolution of hydrochloric acid gas.

The reduction of niobium takes place at a lower temperature than that of tantalum.

Properties.—Black powder, which is carried through the filter by pure water: this inconvenience may, however, be prevented by the addition of alcohol. When heated in the air, it is converted into niobic acid. Nitric acid and aqua-regia have no effect upon it; but a mixture of hydrofluoric and nitric acid attacks it at ordinary temperatures. If we assume that the composition of niobic acid is analogous to that of tantalic acid, the atomic weight of niobium will be greater than that of tantalum.

Compounds of Niobium.

NIOBIUM AND OXYGEN.

NIOBIC ACID. NiO^3?

Preparation.—The acid prepared from Bavarian tantalite is mixed with charcoal and heated in a current of chlorine gas. By this treatment it is converted into a yellow, very fusible, and volatile chloride, and a white chloride which is infusible and but slightly volatile. The two chlorides when immersed in separate portions of water, are converted into oxygen-acids and hydrochloric acid. The hydrochloric acid is then removed by boiling the mixture and washing the insoluble residues with water. The acid obtained from the infusible white chloride is again mixed with charcoal and exposed to a current of chlorine, and the white chloride obtained, kept distinct as before from the volatile yellow chloride; the latter decreases in quantity on each repetition of the process. Nevertheless, Rose did not succeed in obtaining a perfectly colourless chloride entirely free from the yellow compound, even after repeating the above operation a great number of times. The white chloride itself, however, is partially volatile, and on freeing it by sublimation, first from the yellow chloride, and afterwards from the non-volatile white portion, and then digesting in water as above, an acid is obtained, which yields an almost colourless and perfectly volatile chloride. This is the *Chloride of Niobium.* The fixed white residue appears to be a compound of the chloride with the oxygen-acid of the other metal; for, if mixed with charcoal and treated with chlorine, it yields a large quantity of yellow chloride with a small residue of the white compound; and if this compound is again submitted to the same process, it yields similar results, till at last little or no residue remains. Rose has observed similar phenomena on treating the pure tantalic acid obtained from the tantalite of Finland with charcoal and chlorine; and finds that the formation of the fixed white compound may, in this case, be entirely prevented by excluding air and moisture. Chloride of tungsten, under the same circumstances, likewise yields a fixed white residue, which is resolved by heat into red chloride of tungsten and tungstic acid.

The acid obtained from the yellow chloride of the mineral from Bodenmais, Rose calls *Pelopic Acid,* and the metal itself *Pelopium.* (See next Chapter.)

Properties.—Colourless, both in the hydrated and anhydrous state: the hydrated acid, like tantalic acid, becomes incandescent during its transition into the anhydrous state. When heated, it acquires a yellow colour, much deeper than that of tantalic acid under the same circumstances: on cooling, it again becomes colourless. After ignition, it appears in fragments having a high degree of lustre, whereas tantalic acid forms a dull powder. When ignited in a current of ammoniacal gas, it turns black, and yields a large quantity of water: in a current of hydrosulphuric acid, it is slowly converted into sulphide of niobium. The specific gravity of niobic acid is considerably lower than that of tantalic acid, and moreover is subject to the same remarkable variations, and from the same causes: *e. g.*, specific gravity of the amorphous acid, prepared by decomposing the chloride with water, after it had been exposed to the air for a considerable time, and igniting over a spirit lamp; (1) = 5·12; (2) = 4·977; after exposure to the intense heat of a charcoal fire, (1) = 4·5612; (2) = 4·562 at 20°; in the porcelain-furnace, the acid was converted into a loosely coherent mass, easily reduced to a sandy powder, and in this state had a specific gravity (1) = 4·6; (2) = 4·602 at 20°; specific gravity of niobic acid prepared from the chloride without previous exposure to the air = 5·257; after exposure to a charcoal fire for four hours, 4·581 at 20°; after ignition in a porcelain-furnace, 4·589 at 15°; specific gravity of niobic acid obtained from North American Columbite = 5·259 at 10°; after ignition in the porcelain-furnace and subsequent pulverization, the powder had a specific gravity of 4·601; niobic acid from the Samarskite of Siberia = 5·262 at 13°; after heating in a porcelain-furnace, 4·626 at 12°. Amorphous niobic acid varies in density between 5·2545 and 5·2620, the crystalline acid between 4·664 and 4·7633. The mean densities of the two varieties are to one another as 1 : 0·875. Niobic acid is insoluble in all reagents after ignition.

Combinations.—*a.* With Water.—Niobic acid is thrown down from its alkaline solutions by acids,—but most completely by sulphuric acid, even at ordinary temperatures—in the form of white hydrate.

b. With Acids. Hydrated niobic acid is sparingly soluble in hydrochloric acid, so that when an alkaline solution of niobic acid is precipitated by a large excess of hydrochloric acid, the filtrate retains traces of the acid in solution. Niobic acid is soluble to a certain extent in oxalic acid, and probably also in hydrofluoric acid. The ignited acid likewise dissolves in fused bisulphate of potash or ammonia, forming a mobile liquid, which in the former case becomes crystalline on cooling, and in the latter—provided the sulphuric is in excess—forms a clear, thick syrup.

c. With Salifiable Bases.—Niobic acid expels carbonic acid from carbonate of soda when fused with it; and it is remarkable that the quantity of oxygen expelled from the carbonic acid is more than double of that which is contained in the niobic acid itself. The resulting salt is more fusible than the corresponding tantalate. Niobic acid, like tantalic acid and pelopic acid, is remarkable for forming, when fused with alkaline carbonates, acid salts, which are more or less insoluble in water, but dissolve in solution of potash or carbonate of potash; but if the fusion be sufficiently prolonged, the resulting salt is completely soluble in pure water, which is not the case either with tantalic or pelopic acid.

Alkaline Niobiates are soluble in water, in solution of potash, and in carbonate of potash, but dissolve with great difficulty in excess of soda and carbonate of soda; niobiate of soda indeed is much less soluble in these reagents even than tantalate of soda. Niobic acid is precipitated from its alkaline compounds by acids, especially by sulphuric acid, even at ordinary temperatures—unlike tantalic acid, which requires the aid of heat. Oxalic acid does not affect alkaline niobiates; but acetic acid, chloride of ammonium, and a current of carbonic acid gas, produce a precipitate—soluble in the latter case in a large quantity of water.

Niobiate of soda acidulated with sulphuric or hydrochloric acid, and treated with infusion of galls, deposits a deep orange-red precipitate, somewhat like that formed by titanic acid. This precipitate is soluble in alkalis, and is not produced in the presence of fixed organic acids. Ferrocyanide of potassium, added to a solution of niobiate of soda acidulated with sulphuric acid, forms a deep red precipitate somewhat like that thrown down from an acid solution of niobic acid itself by solution of galls. The precipitate is slightly soluble in a large excess of hydrochloric acid. Ferricyanide of potassium gives a bright yellow precipitate with niobiate of soda. If a solution of the same salt be mixed with sulphuric or hydrochloric acid, and a piece of zinc immersed in it, a precipitate is obtained having a beautiful blue colour; the more acid the solution, the more rapidly is the precipitate deposited. After a while, however, the blue colour becomes dingy, and finally brown.

Niobium and Sulphur.

A. Sulphide of Niobium.—Formed by decomposing chloride of niobium or niobiate of soda by a current of dry hydrosulphuric acid gas with the aid of heat. Crystalline; black; decomposed by chlorine at ordinary temperatures.

B. Basic Sulphate of Niobic Acid.—When niobic acid is fused with bisulphate of potash or ammonia, the niobic acid obtained from the fused mass is intimately combined with a portion of sulphuric acid: to free it from this, it is necessary to wash the niobic acid, first with pure water and then with water containing ammonia.

Niobium and Chlorine.

Chloride of Niobium.—This compound is formed at a lower temperature than chloride of tantalum or chloride of pelopium, though it is less volatile than either; hence it is more easily reduced, whether alone or in combination. It dissolves completely in sulphuric acid with the aid of a gentle heat: the solution is not rendered cloudy by boiling; but if diluted with water and then boiled, it becomes turbid, and ultimately deposits the whole of the niobium in the form of niobic acid. When treated with hydrochloric acid, it neither dissolves nor forms a jelly; and the addition of water does not produce any change. Dilute hydrochloric acid behaves in the same manner; but, on the addition of water, a clear solution is obtained, which does not deposit niobic acid on boiling, but is rendered turbid by sulphuric acid at ordinary temperatures. It is completely decomposed by a large quantity of boiling water; a milky liquid being formed, from which niobic acid is precipitated in flakes by boiling. Caustic potash dissolves it completely, so likewise does a boiling solution of carbonate of potash. Hydrosulphuric acid does not attack it at ordinary temperatures, but readily converts it into sulphide of niobium, when aided by heat.

Niobium and Potassium.

Niobiate of Potash and Carbonate of Potash.—On fusing niobic acid with carbonate of potash, a double salt of niobiate and carbonate of potash is formed, from which the carbonate may be separated by keeping the temperature low, and arresting the process before the whole of the carbonic acid is expelled. On digesting in water, an insoluble acid salt of potash is obtained. The latter is soluble in solution of potash.

NIOBIUM AND SODIUM.

NIOBIATE OF SODA.—*a. Mononiobiate.*—Niobic acid when fused with soda forms a compound which is soluble in water, especially at a boiling heat. The solution is not decomposed either by continued boiling or by slow evaporation. The salt may be rendered anhydrous without losing its solubility. A strong solution of niobiate of soda gives a crystalline precipitate with caustic soda and carbonate of soda. The salt is decomposed at a red heat by hydrosulphuric acid gas, the product being a black mass, which is resolved by water into sulphide of hydrogen and sodium, and insoluble sulphide of niobium.

b. Acid Niobiate of Soda.—Obtained like the acid niobiate of potash.

c. With borax, niobic acid yields a colourless bead, which, if the acid is in sufficient quantity, becomes opaque on flaming. In the inner flame, the bead assumes a greyish blue colour, provided it contains a sufficient quantity of acid to produce opacity on cooling.

d. Niobic acid dissolves in large quantity in microcosmic salt, and forms a colourless bead in the outer flame; in the inner flame, a violet-colour is produced; and if the bead be saturated with the acid, it assumes a beautiful blue colour. The colour disappears in the outer flame; the addition of ferrous sulphate changes the blue colour to blood-red. When mixed with tungstic acid—*e. g.*, as obtained from Samarskite—it imparts both to borax and microcosmic salt a yellow colour which disappears on cooling.

NIOBIUM AND YTTRIUM.

Samarskite.—This mineral, first named *Urano-tantalite* or *Columbite*, and afterwards called *Yttro-ilmenite* by Hermann, and *Samarskite* by Rose, is found in the Ilmengebirg in Siberia. Specific gravity = 5·617 (H. Rose); 5·6142 (Wornam); specific gravity of Yttro-ilmenite = 5·398 ....5·45 (Hermann). Fracture conchoidal, with a high lustre, almost metallic. Decrepitates when heated, exhibiting vivid incandescence, and is afterwards perfectly insoluble in hydrochloric acid. Does not change colour when heated in a close vessel; in contact with air it acquires a brownish colour on the outside. (*Pogg.* 72, 471.) The metallic acid obtained from this mineral consists almost wholly of niobic acid, with small quantities of tungstic acid and pelopic acid: hence niobic acid may be obtained from it in a state of greater purity than from the columbites of Bodenmais and North America.

Penetz.

	Columbite.		*Samarskite.* From Siberia. 1.		*Samarskite.* 2.		*Yttro-ilmen*
CaO	0·76				2·08		
MgO	3·01		0·75				2·44
FeO	12·76		15·94		8·06		8·50
MnO } YO	4·48	+ CaO	1·88	MnO	1·00		6·09
YO			8·36		19·74		2·00
U^2O^3	0·56		16·77	UO	5·64		0·50
CuO	·01						
TiO^3					1·50		
HO					1·66		
NiO^3	78·59		55·91		61·33	$+ WO^3$	80·47
	100·17		99·61		101·01		100·00

The large quantity of magnesia found in the Siberian columbite distinguishes it from all other tantalites. Yttro-ilmenite (included by Rose under the name of Samarskite) was examined by Hermann, and supposed by him to contain the acid of a new metal, *Ilmenium.* This acid, however, has been proved by Rose to consist of niobic acid mixed with a small quantity of tungstic acid, to which are owing the peculiarities that induced Hermann to suppose the existence of a new and distinct metal. (*Vid. Pogg.* 73, 455.)

¶ CHAPTER XVII. (B.)

PELOPIUM.

H. Rose. *Pogg.* 63, 377, &c., &c.

History. Given in connection with that of niobium.

Sources. As pelopic acid, more or less mixed with niobic acid, in the tantalites of Bavaria and of North America, but more especially in the former.

Preparation. Similar to that of niobium, by passing a current of dry ammoniacal gas over chloride of pelopium. This salt requires greater heat for its reduction than chloride of niobium.

Properties. Black powder, resembling metallic tantalum in appearance. This resemblance between pelopium and tantalum runs through all their compounds, so that they are very difficult to distinguish; and when they occur together, cannot be separated by any known method.

The atomic weight of pelopium has not yet been determined.

Compounds of Pelopium.

PELOPIUM AND OXYGEN.

PELOPIC ACID. PeO^3?

Preparation. The more volatile yellow chloride obtained from Bavarian tantalite in the preparation of niobic acid, is similarly treated with water, and the resulting acid washed, dried, and ignited over a spirit-lamp.

Properties. Resembles tantalic acid very closely in all its properties. Colourless at ordinary temperatures. When ignited, it acquires a yellow colour intermediate in depth between that of tantalic and that of niobic acid; becomes colourless again on cooling. Like niobic acid, it is darkened by a current of hydrogen at a red heat, though not so strongly;

when ignited in the air it again becomes white. A current of dry ammoniacal gas likewise blackens it at a red heat, a large quantity of water being formed at the same time. When ignited in a current of hydrosulphuric acid gas, it is slowly converted into sulphide of pelopium. Pelopic acid, like tantalic and niobic acid, varies in density according to the temperature at which it has been ignited: thus, the density of pelopic acid prepared from the chloride and ignited over a spirit-lamp, was found to be (1) = 5·98; (2) = 5·982 at 20°; after exposure to a strong charcoal fire for six hours, and reduction of the semi-fused mass to powder in an agate mortar, the specific gravity of the powder was (1) = 6·361; (2) 6·370 at 20°; after ignition in a porcelain furnace and reduction to powder as before—the powder under the microscope having a crystalline appearance—the specific gravity was: (1) and (2) = 5·793 at 22°. The acid, after exposure to the heat of the porcelain furnace, re-fusion in bisulphate of potash—in which, under these circumstances, it dissolves with great difficulty,—washing with a large quantity of hot water, and then with water containing ammonia, till the filtered liquid no longer rendered baryta salts turbid, appeared very bulky, and had a specific gravity of (1) 6·140; (2) 6·146, after heating in a charcoal fire; (1) and (2) = 6·4825; and lastly, after re-exposure to the porcelain furnace, whereby it became caked together, and exhibited the same properties as before, its density was reduced to 5·830. Pelopic acid prepared from chloride of pelopium which had not been exposed to the air, and having an amorphous appearance under the microscope, had a specific gravity of 6·236 at 15°; after heating in a charcoal fire for one hour, its density was increased to 6·416; and after exposure for three hours longer, to 6·725, the acid still retaining its amorphous state. A portion of acid prepared from the chloride after exposure to the air for two months, decrepitated strongly and became incandescent when heated—appeared crystalline under the microscope—and had a specific gravity of 6·239, or nearly the same as the amorphous acid. Pelopic acid obtained by the decomposition of the acid chloride, and found in the tube used in the preparation of chloride of pelopium, had the lowest specific gravity yet found, *viz.*, 5·495 at 15°; and after exposure for an hour to a charcoal fire, 5·566; this acid appeared under the microscope to consist of distinct acicular crystals. Pelopic acid from North American Columbite, prepared from the chloride, had a specific gravity of 6·098; and after ignition in a porcelain furnace—whereby it became caked together, and appeared under the microscope to consist of large crystals—the specific gravity was increased to 6·17. From these results, Rose concludes that pelopic acid is susceptible of three modifications: (1) amorphous; (2) crystalline before ignition; (3) crystalline after ignition in the porcelain-furnace. The specific gravity of (1) and (2) varies according to the mode of their preparation; that of (3) is constant. The range of specific gravity for pelopic acid appears to be between 5·495 and 6·725. From this it will be seen that its density is intermediate between that of tantalic and that of niobic acid. It is insoluble in all reagents after ignition, unless previously fused with bisulphate of potash (or alkaline carbonates?).

Of the three acids, niobic is the strongest and most easily reduced, tantalic acid the weakest and least easily reduced to the metallic state, pelopic acid occupying the intermediate position.

Combinations.—*a.* With water. Obtained in the same manner as hydrated tantalic and niobic acid. Sulphuric acid precipitates it less completely than niobic acid. White; amorphous.

b. With Acids. Hydrated pelopic acid is more soluble in hydrochloric acid than niobic acid; the solution appears opalescent, and is completely precipitated by boiling with sulphuric acid. Pelopic acid likewise dissolves in fused bisulphate of potash: the mass does not appear crystalline on cooling, as in the case of niobic acid.

c. With Salifiable Bases. Pelopic acid, like tantalic and niobic acid, when fused with excess of carbonate of soda, expels a quantity of carbonic acid much larger than that which corresponds to its own amount of oxygen. It likewise forms acid salts by fusion with alkaline carbonates; but the quantity of acid pelopiate produced is smaller than the quantity of acid tantalate formed by the action of tantalic acid on alkaline carbonates. These acid salts are insoluble in water, but dissolve in excess of potash or carbonate of potash.

Alkaline Pelopiates are soluble in water, and likewise in potash or its carbonate, but are precipitated from a strong solution by soda and carbonate of soda. They are precipitated by the same reagents as niobic acid (p. 17). When acidulated with sulphuric or hydrochloric acid, they yield an orange-yellow precipitate with tincture of galls, and a brownish-red precipitate with ferrocyanide of potassium. Alkaline pelopiates, when mixed with a large excess of hydrochloric acid, are precipitated at first, and the precipitate afterwards redissolved, an opalescent solution being obtained, which, unlike tantalic acid, is completely precipitated by sulphuric acid at a boiling heat. A neutral solution of pelopiate of soda does not become turbid on exposure to the air (a peculiarity which serves to distinguish pelopic from tantalic acid). When a piece of zinc is immersed in the solution of an alkaline pelopiate strongly acidulated with hydrochloric acid, the precipitated acid does not assume a blue colour, but only appears a little less white or slightly grey: on adding sulphuric acid, however, it acquires a pure blue colour, which, after some time, grows dull, but does not change to brown. A beautiful blue colour is obtained by treating chloride of pelopium with hydrochloric acid, diluting with water, and adding a piece of zinc.

PELOPIUM AND SULPHUR.

A. SULPHIDE OF PELOPIUM.—Obtained in a similar manner to the sulphide of niobium; but the decomposition is effected at ordinary temperatures. Black. Not attacked by chlorine at ordinary temperatures, but decomposed on the application of heat.

B. BASIC SULPHATE OF PELOPIC ACID.—Formed under the same circumstances as the corresponding niobium compound. Decomposed likewise by prolonged washing, especially with water containing ammonia.

PELOPIUM AND CHLORINE.

CHLORIDE OF PELOPIUM.—Produced at a lower temperature than chloride of tantalum. Chloride of pelopium has a great tendency to combine with pelopic acid; and in preparing it from pelopic acid, charcoal, &c. (p. 16), it is necessary to place a layer of pure charcoal beyond the mixture to prevent this combination. Chloride of pelopium volatilizes at 125° and fuses at 212° C.; hence, like chloride of tantalum, it begins to volatilize before fusion. The pure salt forms a clear yellow liquid, which solidifies more slowly than fused chloride of tantalum. It dissolves in sulphuric acid, forming a solution which is similar in its properties to that obtained with chloride of tantalum, excepting that the jelly formed on boiling is less dense. It likewise dissolves in hydrochloric acid at ordinary temperatures; but if it be treated with boiling hydrochloric acid, and the mixture when cold diluted with water, a clear solution is obtained, which is not precipitated by boiling or by sulphuric acid at ordinary temperatures. It is decomposed by boiling water; but the resulting acid is not of a floculent appearance, and is very difficult to collect on a filter. It is much more soluble both in caustic potash and its carbonate, than chloride of tantalum. It is blackened and decomposed by hydrosulphuric acid at ordinary temperatures.

PELOPIUM AND POTASSIUM.

ACID PELOPIATE OF POTASH.—By fusing pelopic acid with carbonate of potash, and treating the residue with water, an insoluble acid salt is obtained, though in much smaller quantity than in the case of tantalic acid. The salt is soluble in solution of potash.

PELOPIUM AND SODIUM.

PELOPIATE OF SODA.—*a. Neutral salt.* When pelopic acid is fused with excess of carbonate of soda, and the fused mass treated with water, the solution—as in the case of the other two acids—does not contain a trace of pelopic acid; but on again adding a large quantity of water, an opalescent solution is formed, less turbid than with tantalate of soda. Pelopiate of soda is less stable than the corresponding salt of niobic acid; for on boiling its aqueous solution, a white precipitate is formed—less considerable, however, than with tantalate of soda. When a cold solution of this salt is treated with caustic soda, and the mixture evaporated over oil of vitriol, a mass is obtained which does not again dissolve completely in boiling water; but this character is not so well marked as with the tantalate of soda. A strong solution of pelopiate of soda is precipitated by caustic soda or carbonate of soda; and if the mixture be slowly and carefully made, the salt is obtained in the crystalline state, though the crystals are less distinct than in the corresponding niobium compound. It is decomposed by hydrosulphuric acid in a similar manner to niobiate of soda.

b. Acid Salt.—Obtained in a similar manner to the acid salt of potash, and likewise by boiling a solution of the pelopiate. It is decomposed by a current of hydrosulphuric acid at a red heat, the mass becoming black in consequence of the formation of sulphide of pelopium; on cooling, the decomposed mass exhibits a deep brown colour.

c. With borax, pelopic acid behaves in a precisely similar manner to tantalic acid.

d. Microcosmic salt dissolves pelopic acid in large quantity, forming a colourless bead in the outer flame. In the inner flame, the bead assumes a clear brown colour slightly tinged with violet; in the oxidizing flame, the colour disappears again after some time. If sulphate of ferrous oxide is added to the brown bead, it assumes a crimson colour.

A mixture of niobic and pelopic acids—as obtained, for instance, from the tantalite of Bodenmais—generally communicates a brown colour to microcosmic salt in the inner flame. ¶

CHAPTER XVIII.

TUNGSTEN.

Scheele: *Opusc.* 2, 119.
De Luyart (The brothers). *Chemische Zergliederung des Wolframs, &c.* translated by Gren. *Halle,* 1786.
Klaproth. *Beiträge,* 3, 44.
Vauquelin & Hecht. *Journ. des Mines,* 19, 3.
Richter. *Ueber die neuern Gegenstände der Chemie,* 1, 45; 10, 148.
Bucholz. *Schw.* 3, 1.
Berzelius. *Schw.* 16, 476.—Also *Ann. Chim. Phys.* 17, 13.—Also *Pogg.* 4, 147; 8, 267.
Wöhler. *Pogg.* 2, 345.
Malaguti. *Ann. Chim. Phys.* 60, 271; also *J. pr. Chem.* 8, 179.
Anthon. *J. pr. Chem.* 8, 399; 9, 6, 8, & 337.
Margueritté. *J. Pharm.* 3, 7, 222.

Wolfram, Tungstène, Scheel, Scheelium, Wolframium.

History. Tungstic acid was discovered by Scheele, in 1781; metallic tungsten was first obtained from it by the brothers De Luyart. Its combinations were principally examined by Berzelius.

Sources. As tungstic acid and some of its salts in Tungstite, tungstate of lead, and Wolfram (unless the latter contains suboxide of tungsten), and in small quantities in Yttro-tantalite.

Preparation. 1. By exposing tungstic acid mixed with powdered charcoal in a covered crucible to the strongest heat of a powerful blast furnace (De Luyart); or by strongly igniting tungstate of ammonia in a charcoal crucible. (Bucholz.) The metal is rarely obtained in large grains.—2. Hydrogen gas is passed over ignited tungstic acid containing potash as long as oxygen given off, and the reduced metal is boiled with solution of potash, which dissolves out the adhering tungstate of potash. (Wöhler.)—3. At a strong red heat, pure tungstic acid may likewise be reduced by hydrogen gas. (Berzelius.)—4. With carbonate of soda on charcoal, tungstic acid may also be easily reduced in the inner blowpipe flame. (Berzelius.)—5. Children succeeded in reducing tungstic acid by means of his voltaic battery.—6. Clarke obtained from tungstic acid, before the oxy-hydrogen blowpipe flame, a copper-coloured(?) metal.

Properties. The metal, as obtained by the first method, is steel-grey, and has a rather powerful metallic lustre; its specific gravity is 17·22 (Allen & Aiken), 17·4 (Bucholz), 17·6 (De Luyart). It is very hard, being scarcely scratched by a file; brittle; barely fusible in a blast-furnace —less readily even than manganese. It is not magnetic.—The metal prepared by the second method is a tin-white, heavy powder: that obtained by the third and fourth methods is a steel-grey, heavy metallic powder; and that obtained by the fifth method is greyish white, brilliant, and very brittle.

Compounds of Tungsten.

TUNGSTEN AND OXYGEN.

A. TUNGSTOUS OXIDE. BROWN OXIDE OF TUNGSTEN. WO^2.

Preparation. 1. Hydrogen gas is passed over tungstic acid free from potash, and feebly ignited in a glass tube. (Berzelius.)—2. Tungstic acid is heated to redness with a small quantity of finely divided charcoal in a covered crucible. (Bucholz, Wöhler.)—3. A mixture of tungstate of potash with excess of sal-ammoniac, obtained by evaporating the mixed aqueous solutions of the salts to dryness, is fused in an earthen crucible till the whole of the sal-ammoniac is expelled; the chloride of potassium is then removed by water; the acid tungstate of potash which remains undecomposed dissolved out by a boiling dilute solution of potash, and the residue well washed with water. (Wöhler.)—4. Dilute hydrochloric acid is made to act on a mixture of tungstic acid and zinc—the zinc and hydrochloric acid being renewed till the whole of the tungstic acid is converted into copper-coloured scales. These scales are then purified with water, out of contact of air, and preserved under water. (Wöhler.)—5. Bichloride of tungsten is decomposed by water. (Wöhler.)

Properties. The oxide prepared by the first and second methods is a brown powder, leaving a dark copper-coloured streak; that obtained by the third method is a jet-black powder, which, under the burnishing steel, becomes grey and assumes the metallic lustre; the fourth method yields the oxide in copper-coloured laminæ, having a metallic lustre; the oxide prepared by the fifth method is violet-brown. Sp. gr.=12·1109. (Karsten.)

Calculation according to Berzelius.

W	96	....	85·7
2O	16	....	14·3
WO^2	112	....	100·0

Decomposition. By strong ignition in a current of hydrogen gas (and if potash is present, even at a lower temperature), this oxide is resolved into metallic tungsten and water; by ignition with dry carbonate of soda out of contact of air, into tungsten and tungstate of soda. (Wöhler.)

B. TUNGSTIC OXIDE. BLUE OXIDE OF TUNGSTEN.

Formed by the action of various deoxidizing agents on tungstic acid.—1. By igniting tungstate of ammonia in a covered crucible. According to Malaguti, a variable quantity of tungstic acid remains mixed with the blue oxide.—2. By passing hydrogen gas over tungstic acid heated in a glass tube by a spirit-lamp, as long as water continues to be given off. The tungstic acid thus treated loses 3·054 per cent. of oxygen. (Malaguti.) According to Malaguti, the brown oxide is never produced at the comparatively low temperature of the spirit-lamp, as long as the stream of hydrogen is kept up; this statement, however, is opposed to that of Berzelius.—3. Carbonic oxide reduces tungstic acid at a red heat to blue oxide. (Göbel; Gmelin.)

Blackish indigo-blue; opaque.

Calculation, according to Malaguti.

2W	192	....	82·76
5O	40	....	17·24
$W^2O^5 = WO^2,WO^3$	232	....	100·00

C. Tungstic Acid. WO^3.

Scheelsäure, Wolframsäure, Acide tungstique.—Found native.

Formation. 1. Tungsten does not oxidise in the air at ordinary temperatures; but at a red heat it takes fire, and, if in a state of powder, burns like tinder, producing tungstic acid. Under these circumstances 100 parts of tungsten absorb 24 parts of oxygen. (De Luyart.) Nitric acid and aqua-regia oxidize tungsten and convert it into tungstic acid. Water, hydrochloric acid, and sulphuric acid do not act on the metal. (De Luyart.)—2. The brown oxide prepared by either of the first three methods remains unchanged in the air at ordinary temperatures, but burns like tinder when heated, and forms tungstic acid (Berzelius, Wöhler); that prepared by the fourth method oxidizes rapidly in the air even at ordinary temperatures, first yielding blue oxide and then yellow tungstic acid. (Wöhler.) The brown oxide likewise dissolves in a boiling concentrated solution of potash, evolving hydrogen gas and forming tungstate of potash. (Berzelius.)—3. The blue oxide remains unaltered in the air at ordinary temperatures, but gradually absorbs oxygen at a red heat (3·15 per cent., according to Malaguti), by which its blue colour is first changed into green and lastly into the characteristic yellow colour of tungstic acid. It dissolves very slowly in aqueous solutions of the alkalis, after being first converted into tungstic acid by the addition of oxygen derived from the water. (Berzelius.)

Preparation. 1. Finely-pounded wolfram is digested for a long time with rather strong hydrochloric acid—the mixture frequently shaken—the acid renewed—and a portion of nitric acid added towards the end of the process to convert the protoxide of iron still combined with the tungstic acid into sesquioxide, and dissolve it. This process is continued till the acid has removed the whole of the sesquioxides of iron and manganese, and the brown powder is for the most part changed to yellow. The insoluble portion, consisting of tungstic acid, undecomposed wolfram, and quartz, after being well washed, is then shaken up with solution of ammonia, which dissolves the liberated tungstic acid. The crystals of tungstate of ammonia obtained by evaporating the filtered solution, are converted into tungstic acid by ignition in the air.—2. Richter fuses one part of powdered wolfram with 4 parts of nitre (Bucholz uses 2 parts of carbonate of potash); exhausts the mass with water; precipitates tungstate of lime from the filtrate containing tungstate of potash, by adding chloride of calcium; and decomposes the lime-salt, after washing, with nitric acid. The tungstic acid is then separated in the form of powder, and is purified from nitrate of lime by washing with water.—The tungstate of lime must be mixed with a small quantity of water and treated with a large excess of boiling and moderately dilute sulphuric, hydrochloric, or nitric acid (3 parts of water to one of oil of vitriol),—boiled for a quarter of an hour—and the tungstic acid washed till the solution begins to pass turbid through the filter. Or the boiling solution of tungstate of potash may be supersaturated with hydrochloric acid; the mixture boiled for a quarter of an hour; the precipitated tungstic acid washed, dried, and dissolved in ammonia; and crystals of tungstate of ammonia obtained from the filtrate by evaporation. (Anthon.) — In a similar manner, L. Mayer (*Zeitschr. Phys. v. W. 5*, 221) fuses 1 part of powdered wolfram with 1 part of nitre and 2 parts of carbonate of potash, till the mixture enters into tranquil fusion or nearly so; pours out the fused mass: reduces it to powder; dissolves in the smallest possible quantity of water; decants the solution from sesquioxide of iron; agitates it with $\frac{1}{8}$ of its volume of spirit containing 95 per cent. of alcohol, which throws down sesquioxides of iron and manganese (the latter being dissolved as manganic acid); filters; distils off the alcohol; precipitates the tungstic acid by an excess of hydrochloric acid; boils the milky liquid rapidly over an open fire, till it becomes yellow; collects the tungstic acid on a filter; and lastly washes and dries it.—If the heat be too slowly applied, the mixture remains white; the precipitated white powder must be collected on a filter, again dissolved in potash, and after supersaturation with hydrochloric acid, rapidly heated to the boiling point. (Mayer.) It is only when small quantities of material are used in this process that the tungstic acid is obtained yellow; larger quantities remain white. (Wittstein.)—The mixture of wolfram, nitre, and carbonate of potash, must be ignited in a platinum or earthen crucible for about eight hours, till the dark green mass fuses tranquilly and becomes thick, and a portion taken out for trial diffuses itself in water with a dark green colour, the insoluble part no longer feeling gritty when rubbed with a glass stirring rod. If the fusion is not sufficiently prolonged, the whole of the tungstic acid does not combine with the potash, whence a portion is lost. The fused mass is poured out; boiled with eight times its weight of water, to which a small quantity of alcohol is added to precipitate the manganese; and the filtrate precipitated by a quantity of chloride of calcium equal to that of the wolfram used in the first instance. Hydrochloric acid is then added till the liquid becomes strongly acid, in order to redissolve the carbonate of lime which is thrown down at the same time; the precipitated tungstate of lime washed by decantation and subsidence, and boiled with a large excess of hydrochloric acid, for a quarter or half an hour, till the yellow colour of the mixture no longer increases in depth: the tungstic acid is then thrown on a filter, washed, and dried.—If the tungstate of lime is not thoroughly purified from potash by washing, the tungstic acid set free by the hydrochloric acid does not exhibit a yellow colour. (Wittstein, *Repert.* 73, 82.)—[As wolfram is generally mixed with quartz, the tungstic acid prepared by the second method may contain silica, unless it has been previously exhausted by ammonia, filtered, and then ignited.]—3. Berzelius fuses one part of wolfram with 2 parts of carbonate of potash; dissolves the mass in water; filters; precipitates with nitric acid; digests the precipitate (consisting of tungstic acid, nitric acid, potash, and silica), with bihydrosulphate of ammonia, which dissolves the tungstic acid; filters; throws down sulphide of tungsten by nitric acid; washes it with water containing nitric acid, because it is soluble in pure water; dries the precipitate; and converts it by gentle roasting into pure tungstic acid.—4. Wöhler boils the wolfram, after fusion with an aqueous solution of 2 parts of carbonate of potash, and mixes the filtrate, while still hot, with sal-ammoniac. On cooling, tungstate of ammonia crystallizes out; it is then washed with water holding sal-ammoniac in solution (in which it is less soluble than in pure water), and ignited; the tungstic acid thus obtained is contaminated with a small quantity of potash.—5. For this reason it is better, according to Wöhler, to evaporate the alkaline filtrate with the sal-ammoniac to dryness; heat the residue in a hessian crucible till the sal-ammoniac is expelled; and prepare the brown oxide according to the third method (p. 25). This oxide, by ignition in an open vessel, is readily converted into tungstic acid.—6. According to Wöhler, also, a mixture of one part of powdered wolfram with 2 parts of chloride of calcium may be fused in a hessian crucible for an hour; and the mass—after being poured out, cooled, and reduced to powder—boiled with water to dissolve out the chlorides of calcium, iron, and manganese. The tungstate of lime, which remains undissolved, is then to be boiled with concentrated hydrochloric acid to remove the lime; and the insoluble tungstic acid, washed, dissolved in ammonia, filtered, evaporated to dryness, and ignited.—7. From *Tungsten* (native tungstate of lime) tungstic acid may be directly separated by nitric acid.

Properties. Tungstic acid, when separated from any of its salts by boiling with an acid, forms a soft, lemon-yellow powder; when prepared by igniting tungstate of ammonia, it is sulphur-yellow, and retains the crystalline form of the ammoniacal salt. Specific gravity = 5·274 (Herapath), 6·12 (De Luyart), 7·1396 (Karsten). Its colour becomes darker when it is heated.—It is tasteless, and does not redden litmus, at least after ignition. When rubbed up to a fine powder with water, part of it goes through the filter, producing a white milky liquid.—[For its reaction with fluxes, see p. 42.]

			Berzelius.		Bucholz.	De Luyart.	Aiken.
			later.	*earlier.*			
W	96	80	79·768	80·09	80	80·64	86·2
3O	24	20	20·232	19·91	20	19·36	13·8
WO^3	120	100	100·000	100·00	100	100·00	100·0

($WO^3 = 1183 + 3 \, . \, 100 = 1483$. Berzelius.)

Decompositions. Tungstic acid turns green when exposed to the direct rays of the sun. (De Luyart.) Probably, the organic particles and dust diffused in the air may exert a deoxidizing action upon it, so that a small portion of the blue oxide may become mixed with the tungstic acid: the loss of oxygen is, however, so slight, that it is impossible to estimate its amount.—By strong ignition in an earthen crucible, tungstic acid is converted into the blue oxide, which, on being heated to redness in the air, absorbs 2 per cent. of oxygen, and is again converted into yellow tungstic acid. (De Luyart.) [This effect is doubtless produced by the carbonic oxide in the furnace, since the blue oxide may likewise be obtained by igniting tungstic acid in a current of carbonic oxide gas.]—By ignition with sulphur, it is likewise converted into the blue oxide. (De Luyart.) By charcoal, at a low red heat, it is reduced to the brown oxide (by which eans Bucholz first obtained this oxide); at a higher temperature, it is reduced to the metallic state.—By hydrogen gas, at a red heat, it is first reduced to the dark blue oxide, then to the brown oxide, and lastly, at a stronger heat, to metallic tungsten. (Berzelius.)—By potassium or sodium, at a gentle heat, it appears to be reduced, with vivid incandescence, to the metallic state (Gay Lussac & Thénard);—by ignition with cinnabar, to sulphide of tungsten. (Berzelius.)—In contact with zinc and hydrochloric acid, it first assumes a blue, then a black, and then a violet colour, and is finally converted into the copper-coloured oxide. (Wöhler.) Protochloride of tin, boiling vinegar, and other deoxidizing agents, convert tungstic acid into the blue oxide. An aqueous solution of sulphurous acid has no action upon tungsten acid.

Combinations.—a. With Water? (see p. 31, 4).

b. With Acids.—Tungstic acid appears to be insoluble in all acids, excepting concentrated hydrochloric acid and hydrofluoric acid, and but slightly soluble even in those.

c. With Salifiable Bases, yielding the SALTS OF TUNGSTIC ACID; TUNGSTATES.—The alkaline and earthy tungstates are colourless. The salts of tungstic acid have a very high specific gravity. They are fixed in the fire unless the base is volatile. The only salts of tungstic acid that are soluble in water are the tungstates of ammonia, potash, soda, lithia, and magnesia. None of the tungstates are dissolved by alcohol. Those which are soluble in water have a bitter metallic taste, and produce a disagreeable sensation in the throat. Sulphuric, hydrochloric, and nitric acids decompose the tungstates. From the insoluble tungstates they separate either pure tungstic acid in the form of a yellow powder, or a white compound of tungstic acid, the composition of which has not yet been determined with certainty. [That the substance thus separated is tungstic acid, is proved by the following facts. When placed in contact with hydrochloric acid and zinc or iron, it is first converted into the blue oxide and then into the brown oxide, which, on removing the metal, is again converted, by exposure to the air, into yellow tungstic acid; it likewise imparts the characteristic colours to borax and microcosmic salt before the blowpipe (p. 42). The undecomposed tungstates, however, occasionally give similar reactions with the fluxes; though several bases are found to interfere with the result. (Berzelius.)] A solution of tungstate of ammonia, potash, or soda, gives with sulphuric, hydrochloric, nitric, acetic, and phosphoric acid, at ordinary temperatures, a white precipitate, which contains the greater portion of the tungstic acid (a small quantity, however, remains dissolved); the precipitate is not soluble in excess of either of these acids, except the phosphoric. Oxalic, tartaric, and citric acids do not precipitate the above-mentioned alkaline tungstates. The precipitate produced by hydrochloric or nitric acid becomes yellow after the lapse of some time, but more rapidly if the liquid is heated; that produced by sulphuric acid remains white for a longer time, and does not acquire so deep a yellow colour when heated. A solution of an alkaline tungstate supersaturated with sulphuric, hydrochloric, phosphoric, oxalic, or acetic acid, yields, on the introduction of a piece of zinc, a beautiful blue colour, arising from the formation of blue oxide of tungsten; this effect is not produced with nitric, tartaric, or citric acid. (H. Rose.)—A solution of the above-mentioned alkaline tungstates gives, with lime-water, and likewise with salts of baryta, lime, oxide of zinc, oxide of lead, protoxide of mercury, and oxide of silver, white precipitates of tungstate of baryta, &c. After an addition of bihydrosulphate of ammonia, the solution gives with hydrochloric acid, a yellow precipitate of tersulphide of tungsten.

¶ Margueritté (*J. Pharm.* 3^{e} *ser.* 7, 222) describes a peculiar series of alkaline tungstates containing excess of acid (from 2 to 6 atoms to 1 atom of base) which are obtained in the following manner: when hydrated tungstic acid is kept for some time in a moderately concentrated solution of a neutral alkaline tungstate, at a high temperature, a considerable quantity of the acid dissolves; but on cooling, the saturated solution again deposits tungstic acid. If it be now filtered, a second separation of the acid takes place; and lastly, a salt crystallizes out, which differs in form, according to its composition, but may be recrystallized without decomposition. These salts are not decomposed by nitric, hydrochloric, or sulphuric acid at ordinary temperatures, but only on boiling. Those which contain two atoms of acid are less soluble in water than those in which the proportion of acid is greater. On mixing their solutions with caustic alkalis or alkaline carbonates, a precipitate is formed, consisting of hydrated tungstic acid containing alkali, insoluble in an excess of the precipitant at ordinary temperatures, but instantly disappearing on adding the solution of a neutral tungstate. These salts have a strong acid reaction and very bitter taste; when heated, they lose water and become yellow and insoluble. This effect is only produced at temperatures above 220°. ¶

Nature of the Precipitate produced in the Solution of Tungstate of Ammonia, Potash, or Lithia, on the addition of an Acid.

All these precipitates agree in the following particulars: their taste is sweet and bitter at the same time; they redden litmus; dissolve in water, especially when hot, but scarcely at all in water containing any portion of the acid by which they have been precipitated (hence, according to Berzelius, they are precipitated by acids from an aqueous solution); and are turned yellow by boiling with excess of sulphuric, hydrochloric, or nitric acid.

The four following theories concerning the nature of this precipitate are subjoined.

1. Scheele erroneously regarded the precipitate as pure tungstic acid.

2. According to the brothers De Luyart, it is a compound of tungstic acid with small portions of the alkali with which that acid was previously combined, and with the acid used to effect its precipitation. Hence it would appear that the precipitate is a compound of tungstic acid with an alkaline sulphate, hydrochlorate, nitrate, or acetate.

The following precipitates were more particularly examined.

a. Tungstate of Ammonia precipitated by Nitric Acid.—White powder; tastes sweet at first, but afterwards very bitter; reddens litmus. When ignited in closed vessels, it leaves a blue residue; in open vessels it leaves yellow tungstic acid. With potash it evolves ammonia. Turns blue on the addition of sulphuric acid. Dissolves sparingly in water; the solution becomes milky and blue on boiling, and deposits a blue powder. The solution mixed with lime-water disengages an ammoniacal odour and gives a precipitate of tungstate of lime; and the filtrate, after being freed from the excess of lime by a current of carbonic acid gas, and afterwards boiled and filtered, leaves nitrate of lime on evaporation.

b. Tungstate of Potash precipitated by Nitric Acid.—The precipitate tastes sweet and then bitter, and produces an unpleasant sensation in the throat. When heated it evolves nitric acid. The residue is yellow while hot, but white after cooling; insoluble, tasteless, but fusible before the blowpipe. The precipitate turns yellow when treated with sulphuric, hydrochloric, or nitric acid, which removes the potash; when distilled with sulphuric acid, it gives off nitric acid vapours. A solution of this substance in water is not precipitated by a small addition of the above-mentioned acids, even on boiling, though its sweet taste is diminished and its bitterness increased; but a larger quantity of acid added to a boiling solution precipitates yellow tungstic acid. The solution decomposed with lime-water, then filtered, first from tungstate and afterwards from carbonate of lime, and subsequently evaporated, yields a mixture of nitrate of potash and nitrate of lime.

c. Tungstic Acid with Acetic Acid and Potash.—*α*. When an aqueous solution of tungstate of potash is boiled with acetic acid and then left to cool, feathery crystals separate from it. These taste sweet at first, then bitter, and redden litmus. On ignition, they first turn blue, then yellow, and after cooling appear white. An aqueous solution of this compound is precipitated by alcohol. The crystals dissolve in warm acetic acid, producing a blue colour; on cooling, the solution becomes colourless, and deposits on the sides of the vessel the tenacious mass *γ*. If the acetic acid solution of the crystals be boiled for a long time, its colour is destroyed, and it deposits nothing on cooling.

β. If the acetic acid solution is nearly evaporated to dryness, and the acetate of potash removed by repeated washing with alcohol, a very bitter white powder remains, which is neutral to blue or red litmus, behaves in the fire like *α*, and is readily dissolved by water; the solution is turned blue by sulphuric acid, and gives a white precipitate of sulphate of copper.

γ. If the precipitate *b*, produced in a solution of tungstate of potash by nitric acid, is dissolved in boiling acetic acid and then left to cool, it deposits on the sides of the vessel, a white, adhesive, waxy mass, which, after kneading in water, becomes tenacious like bird-lime; in this state it has a greasy and very sweet taste, but after drying, becomes dark grey and solid, and tastes very bitter. It behaves in the fire like *α*. The aqueous solution reddens litmus, turns blue on the addition of sulphuric acid, and precipitates sulphate of copper.

The compounds *α*, *β*, and *γ*, when dissolved in water and treated with lime-water and carbonic acid as in *α*, yield acetate of potash, which, however, in the case of *β*, is mixed with carbonate of potash. [So far De Luyart.]

3. According to Berzelius, the precipitate consists only of tungstic acid combined with a small quantity of the acid used for precipitation, and with water. According to the same authority, the precipitate produced by sulphuric or hydrochloric acid, is white and very soluble in pure water; that produced by nitric acid, yellow and but sparingly soluble.

4. According to Anthon, the precipitate consists of hydrated tungstic acid, which is also formed when the anhydrous yellow tungstic acid is washed for a long time with water, the water at last passing milky through the filter, in consequence of the formation of hydrate of tungstic acid. Anthon examined the precipitate produced by nitric acid. A warm solution of the tungstate of potash or soda remains clear on the addition of nitric acid; but, on cooling, deposits a white, bulky, gelatinous mass, which, when thoroughly washed and dried, appears brilliant, of a yellowish-grey

colour, and translucent, but sometimes black and opaque; it also reddens litmus. The precipitate loses by ignition, 13·5 per cent. (2 At.) of water, and leaves a bluish-black residue, which, after being boiled with nitric acid and subsequently ignited in the air, is converted without alteration in weight, into yellow tungstic acid. [Potash was not sought for.] The precipitate when immersed in water immediately after preparation, frequently assumes a blue colour, the water itself acquiring a violet tint, even without exposure to the direct rays of the sun: if the water contains chlorine, the colouring does not take place. The precipitate, when finely pounded, dissolves in from 250 to 300 parts of cold, and in 30 parts of boiling water; the hot solution becomes turbid on cooling; the cold solution is not clouded by the addition of a strong acid. The precipitate dissolves with effervescence in the alkaline carbonates. (Anthon.)

¶ Laurent (*Ann. Chim. Phys.* 3, 21, 54), from an examination of tungstic acid and its ammoniacal salts, concludes that it is susceptible of at least 5 or 6 modifications, and distinguishes it as *Tungstic* (the ordinary variety), *Paratungstic*, *Metatungstic*, *Isotungstic*, and *Polytungstic* acid, according to its saturating power (similarly to phosphoric acid). *Paratungstic acid* is that which exists in the bitungstates with or without water, and the formula of its salts is, $W^4O^{12}, 2MO$. *Metatungstic acid* is obtained by boiling paratungstate of ammonia for several hours, and afterwards heating the dry salt. The solution when evaporated, yields very soluble octohedrons. It is not precipitated by hydrochloric acid: W^3O^9, MO, with or without water. *Isotungstic acid:* W^2O^6, MO. Prepared by boiling metatungstate of ammonia with excess of ammonia, and heating the dry salt as before. The ammoniacal salt is sparingly soluble in water. The solution deposits isotungstic acid on the addition of acids. *Polytungstic acid:* probably $W^6O^{18}, 3MO$. Formed by treating the yellow acid obtained from wolfram with ammonia, and slowly evaporating the solution; paratungstate and isotungstate of ammonia separate first, and the mother-liquor then separates into two strata, one of which is brown and of a syrupy consistence, and is converted on drying into a readily soluble, crystalline mass. This liquid mixed with boiling hydrochloric acid, yields a white precipitate of polytungstic acid which is not gelatinous, and does not become yellow after boiling. Polytungstic acid is characterized by yielding with ammonia, a very soluble salt which forms a gummy mass on evaporation. ¶

Tungsten and Phosphorus.

Phosphide of Tungsten.—Prepared by Pelletier, but not further examined.

Tungsten and Sulphur.

A. Sulphide of Tungsten.—*a. Bisulphide; Tungstous Sulphide, Sulphotungstous Acid, Wolfram-pyrites.*—1. A mixture of one part of tungstic acid with 6 parts of cinnabar is pressed into an earthen crucible, which is fitted with a cover and placed in a larger crucible filled with charcoal, and the whole strongly ignited for half an hour.—2. Vapour of sulphur or hydrosulphuric acid gas is passed over tungstic acid strongly ignited in a porcelain tube. (Berzelius.) Sulphur ignited with tungstic acid, acts on it but imperfectly. (Berzelius.)

Soft, greyish-black powder, which, when submitted to pressure, acquires the metallic lustre and a steel-grey colour. (Berzelius.)

			Berzelius. 1.	Berzelius. 2.
W	96	75	75·04	74·891
2S	32	25	24·96	25·109
WS^2	128	100	100·00	100·000

After prolonged ignition in the air, it leaves 93·5 per cent. of a brown oxide, which, when very strongly heated, turns green without any change of weight, and must be regarded as tungstic acid. By aqua-regia, it is converted into tungstic and sulphuric acid. (Berzelius, *Ann. Phil.* 3, 245.) At a red heat, it slightly decomposes aqueous vapour, but with greater facility at a higher temperature. (Regnault.)

b. Tersulphide, Tungstic Sulphide, Sulphotungstic acid.—1. Formed by dissolving tungstic acid in bihydrosulphate of potash, and precipitating the solution by an acid.

$$2WO^3 + 3(KO, 2HS) + 3SO^3 = 2WS^3 + 6HO + 3(KO, SO^3).$$

2. By saturating an aqueous solution of tungstate of ammonia with hydrosulphuric acid gas, precipitating by an excess of acid, then washing the precipitate with cold water and drying it. As the tersulphide of tungsten is somewhat soluble in water, the water, after the first yellow liquid has passed through the filter, becomes continually darker in colour, and on evaporation, leaves tersulphide of tungsten in the form of a brown residue less soluble in water than before. If the liver-coloured precipitate is boiled with hydrochloric acid, it becomes darker in colour, and ultimately blackish-blue, from closer aggregation of its particles, but remains soluble in water. (Berzelius.)

The dried precipitate is black, but yields a liver-coloured powder.

When heated in a retort it evolves sulphur, and is converted into bisulphide of tungsten. At the same time it gives off traces of water and hydrosulphuric acid, the latter being either combined with the sulphide of tungsten, or, what is more probable, produced, together with portions of tungstic acid, by the decomposition of the mechanically combined water. A small quantity of hydrosulphuric acid is likewise evolved by merely boiling the sulphide in a retort with water. It dissolves in an aqueous solution of potash or of carbonate of potash (in the latter case without effervescence, because bicarbonate of potash is produced), yielding a dark brown solution, which contains a compound of tersulphide of tungsten with sulphide of potassium, besides tungstate of potash. If the solution is boiled in an open vessel, it attracts oxygen, and becomes lighter in colour, passing through green into yellow. Solution of ammonia dissolves dry tersulphide of tungsten very slowly, but the recently precipitated sulphide somewhat more readily. The alkaline bihydrosulphates dissolve it, with evolution of hydrosulphuric acid. Water dissolves the tersulphide in small quantity, especially with the aid of heat. From the yellow solution, sal-ammoniac and acids precipitate the greater part of the substance. (Berzelius.)

Tersulphide of tungsten forms with the more basic metallic sulphides, a class of compounds called *Sulpho-tungstates*, which generally have the composition, MS,WS^3, the symbol MS representing the more basic metallic sulphide. The compounds with the alkali-metals are obtained by saturating an aqueous solution of the tungstate with hydrosulphuric acid;

$KO,WO^3+4HS = KS,WS^3+4HO$. The last portions of the alkaline tungstate are decomposed with great difficulty by the hydrosulphuric acid. The insoluble sulpho-tungstates are prepared by decomposing a solution of one of the soluble compounds with another metallic salt. The compounds containing the alkali-metals are red and crystallizable, taste of sulphur, and yield a yellow or red solution with water. This solution may contain $MO,HS+WO^3,3HS$. The liquid gradually becomes colourless when exposed to the air, depositing sulphur and tersulphide of tungsten, while tungstate and sulphate of the alkali remain in solution. If the base is in excess, oxidation takes place more rapidly and without separation of insoluble matter. The aqueous solution is still capable of dissolving an additional quantity of tersulphide of tungsten, which colours it deep brown; in this case, a more careful addition of acid is necessary. An excess of acid precipitates the tersulphide of tungsten, with evolution of hydrosulphuric acid and formation of an alkaline salt. Those oxides of the heavy metals which retain their oxygen with but feeble affinity, are decomposed in the solution, producing an alkaline tungstate and a sulphide of the metal employed. (*e.g.* $KS, WS^3 + 4CuO = KO, WO^3 + 4CuS$). (Berzelius.)

B. Tungstate of Tersulphide of Tungsten ?—If an aqueous solution contains an alkaline tungstate and an alkaline sulpho-tungstate together $[MO,WO^3+MS,WS^3]$, the addition of an acid causes the separation of a light, reddish-brown compound, which is not blackened by boiling with hydrochloric acid, but when dry evolves sulphurous acid on ignition, and leaves a greyish blue mixture of bisulphide and blue oxide of tungsten. (Berzelius.)

C. Sulphate of Tungstic Acid ?—Concentrated nitric acid produces in an aqueous solution of tersulphide of tungsten, and sulphuric acid in a solution of tungstate of ammonia, a white heavy precipitate, consisting of sulphuric acid, tungstic acid, and water. On ignition, this compound evolves sulphuric acid, and leaves pure tungstic acid; it likewise dissolves in water, but is again precipitated by nitric or sulphuric acid. (Berzelius.)

Tungsten and Bromine.

A. Oxy-bromide of Tungsten.—Formed by passing vapour of bromine in small quantities over an ignited mixture of tungstic acid and charcoal. Its formula is $W^2O^5+W^2Br^5$.

B. Tungstate of Bromide of Tungsten.—Formed when the same mixture is raised to a higher temperature, and bromine vapour passed over it in greater quantity: WO^3+2WBr^3. (Bonnet, *J. pr. Chem.* 10, 206.)

		A.	Bonnet.			B.	Bonnet.
4W	384	47·06	45·97	3W	288·0	36·81	37
5Br	392	48·04	48·00	6Br	470·4	60·12	60
5O	40	4·90	6·03	3O	24·0	3·07	3
	816	100·00	100·00		782·4	100·00	100

Tungsten and Chlorine.

A. Chloride of Tungsten.—*a. Bichloride.*—Tungsten heated in chlorine gas takes fire and burns with a dull red light, sometimes producing small dark red needles collected together in woolly tufts, sometimes a deep red, dense, fused mass, with glassy fracture. The compound fuses readily and then boils, and is converted into a red vapour darker in colour than nitrous acid. (H. Davy, Wöhler.)

	Calculation.		Malaguti.
W	96·0	57·55	57·61
2Cl	70·8	42·45	42·39
WCl^2	166·8	100·00	100·00

When immersed in water it rapidly assumes a violet colour, and is gradually resolved into brown oxide of tungsten and aqueous hydrochloric acid. (Wöhler.) The product of this action is a blue oxide, which, after being washed and dried, does not, when ignited in the air, absorb 7·1 per cent. of oxygen, as pure tungstous oxide should do, but at most only 3·2 per cent.; probably because, after being separated from the chloride of tungsten, it is converted into a higher oxide by exposure to the air. (Malaguti.)—It dissolves in solution of potash with evolution of hydrogen gas, yielding tungstate and hydrochlorate of potash. With ammonia it behaves in the same manner, excepting that the solution is yellow, and when heated becomes colourless and deposits brown oxide. (Wöhler.)

b. Terchloride.—Dry chlorine gas is passed over heated bisulphide of tungsten. (Wöhler.) For this purpose a tube with five bulbs is used, the end being drawn out to a fine point. The first bulb contains the sulphide of tungsten heated by means of a spirit-lamp. At first a white cloud appears, which condenses into white flakes and is expelled by warming the bulbs. After this, the red compound *b* passes into the second bulb and collects in the form of an oily liquid. Another less volatile compound [which Malaguti regards as terchloride of tungsten: *see below*] is likewise mixed with it. To purify the red compound *b* from this substance, the second, third, and fourth bulbs are warmed in succession, so that it finally collects in the fifth bulb in a state of purity, while the less volatile compound remains behind. The fifth bulb is then separated from the rest by fusion in the flame of a spirit-lamp. (Malaguti.)

Terchloride of tungsten crystallizes in very long, transparent needles of a dark red colour; it fuses readily, and on cooling, recrystallizes in needles which adhere to the glass vessel. It is easily converted into vapour, the colour of which resembles that of hyponitric acid. (Wöhler.)

	Calculation.		Malaguti.
W	96·0	47·48	51·35
3Cl	106·2	52·52	
WCl^3	202·2	100·00	

Malaguti, from his analysis of the compound *b*, deduces the formula W^2Cl^5. Nevertheless, he satisfied himself that when treated with water, in the absence of all oxidizing agents, it is immediately converted into hydrochloric and tungstic acids without any evolution of hydrogen gas;

whereas W^2Cl^6 would necessarily be resolved into hydrochloric acid and blue oxide of tungsten. In the preparation of the compound *b*, a second and less volatile substance is formed, which Malaguti, according to his own analysis, regards as terchloride of tungsten, but which, according to H. Rose's experiments, is a compound of tungstic acid with terchloride of tungsten (described under B). The formation of tungstic acid probably took place because the chlorine which acted on the sulphide of tungsten was not quite free from air or moisture. Probably also the volatilization of the compound *b* from one bulb into the other did not suffice to separate this tungstate of chloride of tungsten completely, so that the compound *b*, when decomposed by water, yielded too large a quantity of tungstic acid, and Malaguti calculated the tungsten accordingly; and as he did not estimate the amount of chlorine, the matter remained unexplained.

Terchloride of tungsten is almost immediately decomposed by exposure to the air (by the action of the moisture present) into hydrochloric and tungstic acids; in water it swells up with a hissing noise and evolution of heat, like lime in the act of slaking, and is almost entirely converted into hydrochloric and tungstic acids. (Wöhler.)

B. Tungstate of Chloride of Tungsten.—Dry chlorine is passed over brown oxide of tungsten heated in the bulb of a glass tube. Under these circumstances, this brown oxide becomes incandescent, whereas the black oxide does not. The bulb becomes filled with dense yellowish vapours which condense into scales. (Wöhler.)

$$3WO^2 + 3Cl = WCl^3, 2WO^3$$

Yellowish white scales, resembling boracic acid; readily volatilized, even before fusion, in dark yellow vapours, which have a pungent odour like that of hydrochloric acid. (Wöhler.)

	Calculation.		H. Rose.	Malaguti.	Bonnet.
3W	288·0	65·13	66·67	46·72	55·2
3Cl	106·2	24·01			40·0
6O	48·0	10·86			4·8
$WCl^3, 2WO^3$	442·2	100·00			100·0

According to Bonnet, the formula should be $2WCl^3, WO^3$. This substance, when strongly heated, is partially resolved into fixed tungstic acid, volatile bichloride of tungsten, and chlorine gas. Hence, a small quantity of bichloride of tungsten (separable by its greater volatility) is formed during the preparation, partial decomposition taking place at the heated sides of the glass bulb. (H. Rose.) When exposed to a damp atmosphere it is converted, in the course of a few hours or days, into hydrochloric acid gas and tungstic acid; water decomposes it rapidly, the products being tungstic and hydrochloric acids. When this compound is volatilized over a spirit-lamp, the aqueous vapour generated by the combustion decomposes the volatile chloride of tungsten, producing vapours of hydrochloric acid, and a luminous smoke, which diffuses itself through the room, and afterwards condenses into thin yellow flakes of tungstic acid. Solution of ammonia dissolves the chloride of tungsten instantaneously, with a hissing noise and great rise of temperature, the products being tungstate and hydrochlorate of ammonia. (Wöhler.)

C. Hydrochlorate of Tungstic Acid.—Highly concentrated hydrochloric acid dissolves tungstic acid in small quantities; water precipitates from the solution a white curdy substance (tungstic acid containing hydrochloric acid?). (Berzelius.) The precipitate obtained by supersaturating a solution of tungstate of ammonia with hydrochloric acid is likewise regarded by Berzelius as a compound of tungstic and hydrochloric acids.

Tungsten and Fluorine.

Fluoride of Tungsten and Hydrofluate of Tungstic Acid.—Tungstic acid after ignition is sparingly dissolved by aqueous hydrofluoric acid; that which is prepared in the wet way forms with hydrofluoric acid a yellow milky liquid soluble in a large quantity of water. The solution, when slowly evaporated, yields a yellow syrup, which, at a higher temperature, gives off a portion of its acid and solidifies to a greenish, fissured mass. This mass is not decomposed when ignited in a close vessel; it redissolves imperfectly in water, forming a milky liquid as above; the insoluble part consists of tungstic acid, which retains a portion of the hydrofluoric acid so obstinately, that the latter can only be expelled by igniting the tungstic acid with lumps of carbonate of ammonia. The solution contains tungstic acid with excess of hydrofluoric acid. Terfluoride of tungsten forms with the more basic metallic fluorides, compounds which have not yet been isolated, and are known only in combination with tungstates of the metallic oxides. (Berzelius.)

Tungsten and Nitrogen.

A. Nitrate of Tungstic Acid.—The lemon-yellow precipitate produced in a solution of tungstate of ammonia by nitric acid must, according to Berzelius, be regarded as thus constituted. It dissolves in pure water, forming a yellow solution, and is again precipitated on the addition of nitric acid.

B. Tungstate of Ammonia.—*a. Monotungstate.*—Obtained in solution by leaving tungstic acid for some time in contact with ammonia. The liquid, added to a solution of chloride of calcium, precipitates monotungstate of lime; but when evaporated, it evolves ammonia and yields the bitungstate. (Anthon.)

b. Bitungstate of Ammonia.—Tungstic acid separated from wolfram by acids, dissolves in ammonia with ease; the ignited acid less readily; and the blue oxide more slowly still.—1. Tungstic acid prepared from wolfram by the first method (p. 26) with hydrochloric acid and aqua-regia, is digested in aqueous ammonia; and the solution filtered and evaporated to the crystallizing point. The solution prepared with the aid of heat, deposits yellow flakes on cooling, which dry up to a yellowish brown, transparent, resinous mass, consisting of tungstic acid and sesquioxide of iron. The liquid filtered from this substance yields pure crystals of the salt. The mother-liquor leaves, on evaporation, a gummy mass (before remarked by Bucholz, and declared to be the pure salt), likewise consisting of tungstate of ammonia, but probably of different composition.—2. When a hot aqueous solution of monotungstate of potash or soda is mixed with sal-ammoniac, ammonia is set free, and, as the liquid cools, bitungstate of ammonia crystallizes out. (Wöhler, Anthon.)

The salt crystallizes in four-sided needles containing water, or in rhombic tables, having an acrid, bitter, metallic taste. According to Anthon, it reddens litmus slightly.

			Berzelius.		Anthon.	Vauq. & Hecht.
	Crystallized.		1.	2.		
NH^3	17	6·18	5·63	6·338	6	78
$2WO^3$	240	87·27	88·80	87·000	87	
$2HO$	18	6·55	5·57	6·662	7	
$NH^4O,2WO^3+Aq.$	275	100·00	100·00	100·000	100	

The crystals do not undergo any alteration in the air. They cannot, however, be rendered anhydrous without decomposition. At a red heat they evolve water, ammonia, and nitrogen gas, and leave blue oxide of tungsten, or, if air is admitted, tungstic acid. (De Luyart.)—They dissolve in 25 or 28 parts of cold water, but not in alcohol. (Anthon.) The aqueous solution evolves ammonia when evaporated, and becomes more acid in consequence. (De Luyart.)—It yields a white precipitate with nitric acid, which, after long standing, or immediately on boiling, becomes yellow. ¶ Margueritté has succeeded in forming two new compounds of tungstic acid with ammonia: the first—$NH^4O, 3WO^3+5HO$—forms octohedral crystals, which melt under water like phosphorus; the second—$NH^4O, 6WO^3+6HO$—separates in definite, scaly crystals. ¶

C. SULPHO-TUNGSTATE OF AMMONIUM.—NH^4S,WS^3.—If a concentrated solution of tungstate of ammonia is saturated with hydrosulphuric acid gas, this compound gradually separates in difficultly soluble, yellowish red crystals. The mother-liquor yields by spontaneous evaporation yellow rectangular tables, which in other respects possess similar characters to the above, and are consequently dimorphous. The crystals decrepitate strongly when heated, evolve water and hydrosulphate of ammonia, and leave grey bisulphide of tungsten, having a metallic lustre and the form of the crystalline fragments after decrepitation. They dissolve more readily in pure water than in water containing a saline substance in solution. The solution is slowly decomposed by exposure to the air. (Berzelius.)

D. FLUORIDE OF TUNGSTEN WITH HYDROFLUATE OF AMMONIA, OR FLUORIDE OF TUNGSTEN AND AMMONIUM.—*Ammonio-fluoride of tungsten.*—Analogous to the corresponding potash-salt, both in external appearance and in composition. (Berzelius.)

TUNGSTEN AND POTASSIUM.

A. TUNGSTATE OF POTASH.—*a. Monotungstate.*—1. Tungstic acid is digested with an equivalent quantity of aqueous caustic potash or carbonate of potash (in the latter case carbonic acid is expelled), the solution filtered, and evaporated to the crystallizing point.—2. One part of carbonate of potash is heated to fusion in an iron crucible, and powdered wolfram thrown into it as long as effervescence continues—for which purpose about one part is necessary. The mass is kept for some time in a state of fusion;

after which it is poured out, broken to pieces, boiled in water, and the solution filtered and evaporated to dryness; the residue is then treated with an equal weight of luke-warm water, which generally leaves a portion of bitungstate of potash undissolved,—then filtered, partially evaporated, and left to crystallize. (Anthon.)

The salt has a rough, bitter taste and strong alkaline reaction; it fuses just below redness, and forms a transparent liquid, which solidifies to a crystalline mass on cooling. Crystallizes from an aqueous solution in hydrated six-sided prisms, with two of their lateral faces broader than the rest; and either having the terminal edges replaced by planes, or acuminated, or with dihedral summits resting on the broader lateral faces. Attracts moisture from the air, and dissolves in an equal weight of cold water and in half its weight of boiling water, the salt *b* often separating, and the solution retaining an excess of potash. Sulphuric, hydrochloric, or nitric acid, produces a white precipitate in a dilute solution of the salt (p. 31); but with a concentrated solution, on boiling, these acids form a yellow precipitate of pure tungstic acid. (Anthon.)

	Anhydrous.			Crystallized.		Anthon.
KO	47·2	28·23	KO	47·2	22·24	22·0
WO^3	120·0	71·77	WO^3	120·0	56·55	57·5
			$5HO$	45·0	21·21	20·5
KO,WO^3	167·2	100·00	$+5Aq.$	212·2	100·00	100·0

b. Bitungstate.—1. To the salt *a*, in a state of fusion, a quantity of tungstic acid is added equal to that which it contains; and the mass when cold is broken up, boiled in a small quantity of water, filtered, and left to crystallize on cooling.—2. To a boiling aqueous solution of caustic potash, carbonate of potash, or monotungstate of potash, tungstic acid is added as long as it dissolves, and the liquid filtered boiling hot and left to cool. The resulting crystalline powder becomes anhydrous when heated.

The anhydrous salt turns yellow when heated, and fuses below redness to a clear yellow liquid, which, on cooling, solidifies in a bluish or greenish mass of crystals. It reddens litmus, and tastes like the salt *a*, but not so strong. The hydrated crystalline powder appears under the microscope to consist of rhombic tabular crystals, which, by replacement of the edges, are converted into hexagonal prisms. The crystals are permanent in the air. They dissolve in 100 parts of water at 16°, and in 8½ parts of boiling water, separating for the most part as the liquid cools. The solution is precipitated white by acids, but not till after some time if largely diluted. (Anthon.)

	Anhydrous.			Crystallized.		Anthon.
KO	47·2	16·43	KO	47·2	15·46	14·25
$2WO^3$	240·0	83·57	$2WO^3$	240·0	78·64	79·75
			$2HO$	18·0	5·90	6·00
$KO,2WO^3$	287·2	100·00	$+2Aq.$	305·2	100·00	100·00

c. Hyper-acid Salt.—When an excess of tungstic acid is fused with hydrate or carbonate of potash, a bluish grey, crystalline, metallic-shining mass is produced; it appears to yield the salt *b* to boiling water. (Anthon.)
¶ Margueritté describes a pentatungstate of potash—$KO,5WO^3 + 8HO$—which forms prismatic crystals. ¶

C. Sulpho-tungstate of Potassium.—KS,WS^3.—Formed by treating tungstate of potash with hydrosulphuric acid, or by dissolving tungstic acid or tersulphide of tungsten in hydrosulphate of potash, or tersulphide of tungsten in caustic potash.—An aqueous solution of monotungstate of potash is saturated with hydrosulphuric acid gas, and the brownish yellow solution evaporated, either in vacuo over potash, or simply by exposure to the air. In the former case, small yellow crystals are obtained; in the latter, pale red, broad, flat, four-sided prisms, with dihedral summits. The crystals are anhydrous. When heated in a close vessel, they fuse without decomposition, and form a dark brown mass, which becomes brownish yellow on cooling. The salt dissolves in water, forming a brownish yellow solution, from which it is precipitated by alcohol, after some time, in delicate, cinnabar-coloured prisms; but the precipitation is not complete, for the salt is also slightly soluble in alcohol. By careful addition of an acid to the aqueous solution, the compound is converted into $KS, 2WS^3$, the dark brown solution of which leaves a black mass on evaporation. (Berzelius.)

	Crystallized.		Berzelius.
K	39·2	19·68	19·91
W	96·0	48·19	46·80
4S	64·0	32·13	
KS, WS^3	199·2	100·00	

¶ Tungstate of Potash and Ammonia.—$NH^4O, KO, 4WO^3+6HO$.—Prepared by Margueritté. ¶

D. Sulpho-tungstate of Potassium with Nitrate of Potash.—$2(KS, WS^3)+KO, NO^5$.—If the solution of monotungstate of potash which is saturated with hydrosulphuric acid, contains nitre—brilliant, ruby-red, transparent, anhydrous crystals are obtained, which remain unaltered after repeated crystallization. The crystals explode like gunpowder just as they begin to melt, and leave a pale yellow mass, from which water extracts sulpho-tungstate of potassium and tungstate of potash, leaving an insoluble residue of bisulphide of tungsten. Sulphuric or hydrochloric acid disengages hydrosulphuric acid gas, and with the aid of heat, nitric oxide also; whereupon, a portion of the precipitated tersulphide of tungsten immediately turns yellow. Hydrated oxide of copper converts the solution of this compound into a solution of nitrate and tungstate of copper, with separation of sulphide of copper. The compound is very soluble in water, and dissolves almost as readily in cold water as in hot. The solution has a deep red colour, and the salt is precipitated from it by alcohol in crystalline grains. (Berzelius.)

Tungsten and Sodium.

A. Tungstate of Soda.—*a. Monotungstate.*—Prepared by dissolving tungstic acid in solution of caustic soda, or by fusing wolfram with carbonate of soda, and exhausting with water. Anthon projects powdered wolfram into fused carbonate of soda as long as it causes effervescence; keeps the mass at a red heat for some time; reduces it to powder when cold; boils it for some time with water; filters the solution; and evaporates to the crystallizing point.—By heating the crystals, the salt may be obtained anhydrous. In this state it is white, opaque, and permanent in the air, and has a bitter, rough, saline taste, and alkaline reaction. It fuses below a red heat, and forms a clear liquid, which solidifies to an opaque, crystalline mass. (Anthon.) Before the blowpipe, the fused salt first becomes blackish blue and afterwards reddish brown. It is not decomposed by ignition in an atmosphere of hydrogen. (Wöhler.) The crystals deposited from an aqueous solution are translucent, of a pearly lustre, and, according to Vauquelin & Hecht, have the form of long, four-sided laminæ, —according to Anthon, of rhombic tables.—The crystals dissolve in 4 parts of cold and in 2 parts of boiling water (Vauquelin & Hecht); in 1·1 pt. of cold and in 0·5 pt. of boiling water (Anthon).

	Anhydrous.			Crystalline.		Anthon.
NaO	31·2	20·63	NaO	31·2	18·44	18·1
WO^3	120·0	79·37	WO^3	120·0	70·92	71·0
			2HO	18·0	10·64	10·9
NaO,WO^3	151·2	100·00	+2Aq.	169·2	100·00	100·0

b. Bitungstate.—1. Formed when tungstic acid is thrown into a fused mass of the salt *a*.—Wöhler adds the tungstic acid as long as it continues to be dissolved, and then allows the mass to cool.—Malaguti, to avoid obtaining an acid salt, uses a smaller quantity of tungstic acid, so that a portion of the salt *a* remains unacted on, and is afterwards dissolved out by boiling water, leaving the salt *b* in the form of scales.—2. A hot solution of caustic soda or of carbonate or monotungstate of soda is completely saturated with tungstic acid; the hot filtrate allowed to crystallize; and the mother-liquor again evaporated, to obtain an additional quantity of crystals. (Anthon.)—¶ 3. An aqueous solution of monotungstate of soda (as obtained by fusing a mixture of wolfram and carbonate of soda, and exhausting with water) is mixed with hydrochloric acid till the precipitated acid is no longer dissolved on agitation. The liquid is then filtered—evaporated—separated from the tungstic acid which first separates—and then from the chloride of sodium—and lastly set aside to crystallize. (Margueritté.) ¶

The fused anhydrous salt obtained by the first method, crystallizes as it cools, forming long needles on the surface. (Wöhler.) In the fused state it forms a transparent, yellowish liquid. (Anthon.)—When ignited in a current of hydrogen gas, it assumes a copper colour, which is at first superficial only, but gradually extends throughout the mass, and on cooling, changes to golden yellow; it appears to be converted by this process into a mixture of the salt *a* with tungstate of tungstous oxide and soda. (Wöhler.)—The crystals deposited from an aqueous solution, which also contain water, are striated rhombohedrons resembling those of nitrate of soda; they are permanent in the air; redden litmus; and have at first a sweet, afterwards a rough, bitter taste, and dissolve in 8 parts of cold water. (Anthon.) [The white unctuous scales which Malaguti obtained by the first method appear to be less soluble.]

	Anhydrous.			Cryst. from water.		Anthon.
NaO	31·2	11·51	NaO	31·2	10·16	9
$2WO^3$	240·0	88·49	$2WO^3$	240·0	78·12	79
			4HO	36·0	11·72	12
$NaO, 2WO^3$	271·2	100·00	+4Aq.	307·2	100·00	100

¶ Margueritté describes this salt as forming laminated crystals which contain 4½ atoms of water, and are decomposed by acids at ordinary temperatures. He also mentions a salt containing 4 atoms of acid = $NaO,4WO^3+3HO$. ¶

Tungstic acid gives with carbonate of soda, on platinum wire before the blowpipe, a transparent, dark yellow glass, which, on cooling, crystallizes to a white or yellowish white opaque mass. By exposure to the inner flame on charcoal, tungsten is reduced. (Berzelius.)

C. Tungstic acid yields with borax, in the outer blowpipe flame, a transparent glass, which remains clear even after gentle flaming; in the inner flame, the glass acquires a yellow colour, darker in proportion to the quantity of tungstic acid present; on cooling, it changes to blood-red. The addition of tin renders the glass milk-white on cooling. (Berzelius.)

D. With microcosmic salt, in the outer flame, tungstic acid gives a colourless or yellowish glass; in the inner flame, a splendid blue. The addition of tin accelerates the appearance of the blue colour. When either alumina or silica is present, the tin is necessary to bring out the colour. If iron is present, the glass assumes a blood-red colour in the inner flame; on the addition of tin, however, this colour changes to green or blue, especially if the substance does not contain too large an excess of tungstic acid. (Berzelius.)

E. SULPHO-TUNGSTITE OF SODIUM?—$NaS,3WS^2$.—The blackish-grey substance, insoluble in water and decomposible by aqua-regia, which, according to Wöhler, remains after igniting a mixture of tungstate of tungstous oxide and soda with sulphur, must be regarded as a compound of this nature (p. 47).

F. SULPHO-TUNGSTATE OF SODIUM.—NaS,WS^3.— Crystallizes with difficulty from a highly concentrated aqueous solution; with greater facility, however, from an alcoholic solution, by spontaneous evaporation. Forms an entangled mass of crystals, which rapidly attract moisture from the air, and become yellow. If an excess of sulphide of sodium is used, a salt equally soluble in alcohol is produced, which soon becomes moist in the air, and oxidizes at the same time. (Berzelius.)

TUNGSTEN AND LITHIUM.

TUNGSTATE OF LITHIA.—*a. Monotungstate.*—1. Tungstic acid, after ignition, is dissolved in a boiling aqueous solution of carbonate of lithia; and the solution, which is but slowly formed, evaporated to the crystallizing point. (C. Gmelin.)—2. Tungstic acid is projected into fused carbonate of lithia as long as effervescence is produced; and the resulting mass dissolved in water and set aside to crystallize. (Anthon.) The salt forms short, thick, oblique rhombic prisms, of a sharp, very sweet, and roughly bitter taste, which dissolve in water with tolerable facility. (C. Gmelin.) Octohedrons apparently, having an alkaline reaction; very soluble in water. (Anthon.)

b. BITUNGSTATE.—Preparation, similar to that of the bitungstate of soda. Crystallizes readily; reddens litmus; and has a saline, bitter, and afterwards somewhat rough taste. Permanent in the air. Rather less soluble in water. (Anthon.)

TUNGSTEN AND BARIUM.

A. TUNGSTATE OF BARYTA. — *a. Monotungstate.*—1. Formed by precipitating a salt of baryta with monotungstate of potash or soda.—2. By boiling recently precipitated carbonate of baryta with hydrated tungstic acid [*i. e.*, with the precipitate produced by nitric acid in a solution of tungstate of soda].—White powder, which emits a strong light, and cakes together when ignited, without undergoing any loss of weight. Decomposed by the stronger acids, and also by potash or soda, both in the wet and in the dry way. With boiling aqueous oxalic acid it forms a solution which becomes turbid as it cools. Insoluble in water and in boiling phosphoric acid. (Anthon.)

	Calculation.		Anthon.
BaO	76·6	38·96	39
WO^3	120·0	61·04	61
BaO, WO^3	196·6	100·00	100

b. Bitungstate.—Formed by precipitating a soluble salt of baryta with bitungstate of potash or soda. The hydrated precipitate is white, but becomes yellowish after ignition, from loss of water. It does not dissolve in cold water, and but very sparingly in boiling water, so that the solution, on cooling, or on the addition of sulphuric acid, becomes slightly clouded. It is partially dissolved when boiled with oxalic acid. (Anthon.)

	After ignition.		Anthon.		*Hydrated.*		Anthon.
BaO	76·6	24·2	24·14	BaO	76·6	21·18	21
$2WO^3$	240·0	75·8	75·86	$2WO^3$	240·0	66·37	66
				5HO	45·0	12·45	13
BaO,$2WO^3$	316·6	100·0	100·00	+5Aq.	361·6	100·00	100

B. SULPHO-TUNGSTATE OF BARIUM.—1. Recently prepared tungstate of baryta is diffused in water, and decomposed by hydrosulphuric acid; the process goes on very slowly. The lemon-yellow solution yields, by spontaneous evaporation, a yellow, transparent mass, of crystalline-laminated texture.—2. Tersulphide of tungsten is dissolved in a boiling aqueous solution of mono-hydrosulphate of baryta. Bi-hydrosulphate of baryta is decomposed but slowly, even at a boiling heat. The yellow solution thus obtained dries up without any signs of crystallization. If it contains an excess of sulphide of tungsten, it leaves a brown varnish. (Berzelius.)

TUNGSTEN AND STRONTIUM.

A. TUNGSTATE OF STRONTIA. — *a. Monotungstate.* —Preparation, similar to that of the baryta-salt. Likewise anhydrous. White, soft to the touch. When ignited, it emits a vivid light, cakes together, and becomes rough and dense. It is insoluble in water, but yields, with boiling aqueous oxalic acid, a solution which becomes milky on cooling, from formation of a precipitate. (Anthon.)

	Calculation.		Anthon.
SrO	52	30·23	30
WO^3	120	69·77	70
SrO,WO^3	172	100·00	100

b. Bitungstate.—Prepared in a similar manner to the corresponding salt of baryta. White powder, which loses water on ignition, and becomes first grey, then bluish, then green, and lastly yellow. It is insoluble in cold water, but dissolves completely in hot water and in aqueous phosphoric or oxalic acid. (Anthon.)

	After ignition.		Anthon.
SrO	52	17·81	17·24
$2WO^3$	240	82·19	82·76
$SrO,2WO^3$	292	100·00	100·00

	Hydrated.		Anthon.
SrO	52	15·43	15
$2WO^3$	240	71·22	72
5HO	45	13·35	13
+5Aq.	337	100·00	100

B. Sulpho-tungstate of Strontium.—SrS,WS^3.—Monotungstate of strontia diffused in water is very readily decomposed by sulphuretted hydrogen. The yellow solution thus obtained yields lemon-yellow, radiated crystals on evaporation. If an additional quantity of sulphide of tungsten is dissolved in the solution, it leaves a brown syrup on evaporation. (Berzelius.)

Tungsten and Calcium.

A. Tungstate of Lime.—Found in nature as *Tungsten.* Tungstate of potash or soda precipitates chloride of calcium completely, even when a slight excess of acid is present. (Anthon.) The precipitate is a white powder. *Tungsten* belongs to the square prismatic system of crystallization, and is found in two different square octohedrons, one more acute, *Fig.* 21, and one less acute, *Fig.* 23. In the first, the e (above) : e'' (below) = 130° 20′; in the latter = 113° 36′. (Hauy.) Specific gravity = 6·04. (Karsten.) Harder than felspar; colourless and transparent. Before the blowpipe, it fuses at the edges to a translucent glass. Dissolves readily in borax, yielding a transparent glass, which, on cooling, rapidly becomes milk-white and crystalline, and is not coloured in the inner flame, even after the addition of tin. With microcosmic salt, in the outer flame, it forms a clear glass, which, when exposed to the inner flame, appears green while hot, and blue after cooling; if tin is added, it assumes a still darker green colour; but, after long exposure to the blast, with a sufficient quantity of tin, its colour becomes greenish yellow and continually paler, because the tungsten is reduced. With carbonate of soda, tungsten forms a white blistered slag, rounded off at the edges. (Berzelius.)

Hydrochloric or nitric acid extracts the base from powdered tungstate of lime, separating yellow tungstic acid. A boiling solution of potash removes tungstic acid from the powder. The salt is insoluble in water.

			Berzelius.	Bucholz & Brandes.	
	Tungsten.		Westmanland.	Schlackenwalde.	Zinnwald.
CaO	28	18·92	19·40	19·06	16·50
WO^3	120	81·08	80·42	18·00	76·50
Impurities				9·00	5·54
CaO,WO^3	148	100·00	99·82	99·06	98·54

B. Sulpho-tungstate of Calcium.—CaS,WS^3.—Prepared in a similar manner to the baryta compound. Forms a pale yellow, amorphous mass, easily soluble in water and alcohol. With an excess of sulphide of tungsten, it yields a reddish brown, uncrystallizable compound, from the solution of which ammonia throws down a light yellow powder. (Berzelius.)

TUNGSTEN AND MAGNESIUM.

A. TUNGSTATE OF MAGNESIA.—When tungstic acid and carbonate of magnesia are boiled in water, the resulting solution yields, on evaporation, small, brilliant scales, which are permanent in the air, readily soluble in water, and have the same taste as other salts of tungstic acid. From a solution of this salt, acids likewise precipitate a white substance, probably a ternary compound.

B. SULPHO-TUNGSTATE OF MAGNESIUM.—Prepared by the same method as the baryta-salt. The solution, which is readily oxidized in the air, dries up in vacuo to a kind of varnish, which readily dissolves both in water and alcohol. If the solution contains a larger quantity of sulphide of tungsten, it yields, on evaporation, a brown amorphous mass. (Berzelius.)

TUNGSTEN AND CERIUM.

SULPHO-TUNGSTATE OF CERIUM.—CeS,WS^3. A solution of sulphotungstate of potassium gives a yellow precipitate with cerous salts; but not till after the lapse of twenty-four hours. (Berzelius.)

TUNGSTEN AND YTTRIUM.

TUNGSTATE OF YTTRIA.—Formed when a salt of yttria is precipitated by monotungstate of soda. White powder, containing 11·6 per cent. of water; its formula is therefore YO,WO^3+2Aq. It is very sparingly soluble in water, but rather more soluble in an aqueous solution of tungstate of soda. (Berlin.)

TUNGSTEN AND ALUMINUM.

TUNGSTATE OF ALUMINA.—Monotungstate of soda precipitates the salts of alumina completely. (Anthon.)

The neutral salts of yttria, glucina, and alumina, are not precipitated by a solution of sulpho-tungstate of potassium. (Berzelius.)

TUNGSTEN AND THORINUM.

TUNGSTATE OF THORINA.—Monotungstate and bitungstate of potash or soda precipitate the salts of thorina in white flakes. (Berzelius.)

TUNGSTEN AND TANTALUM.

TANTALOUS ACID CONTAINING TUNGSTEN?—Obtained by reducing tantalic acid containing tungstic acid. Resembles pure tantalous acid, but is much harder and denser, and readily polished. (Gahn, Berzelius & Eggertz.)

TUNGSTEN AND TUNGSTEN.

A. TUNGSTATE OF TUNGSTOUS OXIDE AND POTASH.—Obtained in a similar manner to the corresponding soda compound. (p. 47.) Small needles, copper-coloured, with a tinge of violet, like sublimed indigo. Yields a blue powder having a coppery cast. (Laurent, *Ann. Chim. Phys.* 67, 219.)

B. SULPHO-TUNGSTATE OF POTASSIUM WITH TUNGSTATE OF POTASH.—This compound is sometimes obtained in the preparation of sulpho-tungstate of potassium. It is also formed by fusing a mixture of monotungstate of potash with sulphur in a covered crucible. The solution yields on evaporation, lemon-yellow rectangular tables, containing 4·5 per cent. of water of crystallization. If the water is expelled by heating the salt, it becomes opaque and deeper in colour, and then fuses at commencing redness, no decomposition taking place, provided the air is excluded. When ignited in a current of hydrogen gas, it does not yield water. Dissolves easily in water. The lemon-yellow solution is coloured reddish-yellow or red by acids, and gives no precipitate either with salts of protoxide of manganese or with alcohol. 100 parts of the anhydrous salt yield, on analysis, 63·64 parts of tungstic acid, and 49·03 parts of sulphate of potash, from which the following formula may be assumed as nearly correct for the crystallized compound: KS,WS^3+KO,WO^3+4Aq. (Berzelius.)

C. FLUORIDE OF TUNGSTEN AND POTASSIUM WITH TUNGSTATE OF POTASH.—(*Wolfram-Fluorkalium.*) KF,WF^3+KO,WO^3+2Aq.—1. Potash is added to hydrofluate of tungstic acid till a permanent precipitate begins to appear. The solution is then evaporated to the crystallizing point. In this process, half the potassium remains in the mother-liquor as fluoride of potassium:

$$2(WO^3,3HF)+4KO = KF,WF^3+KO,WO^3+2KF+6HO.$$

—2. Tungstate of potash is supersaturated with hydrofluoric acid. $2(KO,WO^3)+4HF = KF,WF^3+KO,WO^3+4HO$. The compound crystallizes in large brilliant scales like boracic acid, permanent in the air, and having a bitter and somewhat metallic taste. At a temperature a little above 100° these scales part with 4·58 per cent. of water and become reduced to a fine powder. The powder fuses at a red heat and without decomposition, provided aqueous vapour and silica are excluded: but the platinum crucible acquires a reddish-brown colour from the action of hydrofluoric acid. The fused compound solidifies on cooling to a pale greenish mass. The crystallized salt dissolves with difficulty in cold, but more readily in hot water; it is not decomposed after repeated solution in water or aqueous hydrofluoric acid, and subsequent evaporation. (Berzelius.)

Crystallized; calculated according to Berzelius.			Or:		
KF	57·9	14·65	2K	78·4	19·84
WF^3	152·1	38·49	2W	192·0	48·58
KO	47·2	11·94	4F	74·8	18·93
WO^3	120·0	30·37	4O	32·0	8·10
2Aq.	18·0	4·55	2Aq.	18·0	4·55
	395·2	100·00		395·2	100·00

100 parts of the compound yielded in the analysis made by Berzelius: Potash 24·24, tungstic acid 59·57, hypothetically anhydrous fluoric acid 11·39, water 4·80.

D. TUNGSTATE OF TUNGSTOUS OXIDE AND SODA.—NaO,WO^3+WO^2,WO^3. Dry hydrogen gas is passed over red-hot bitungstate of soda as long as water continues to be formed, and the monotungstate of soda removed by solution in water. (Wöhler.) 100 parts of bitungstate of soda thus treated, lose on the average 1·576 parts of oxygen, and yield 1·82 parts of water; or 2 atoms of the bitungstate of soda lose one atom of oxygen, and are resolved into one atom of monotungstate of soda and the double salt: (Malaguti.)

$$2(NaO,2WO^3) + H = NaO,WO^3 + (NaO,WO^3 + WO^2WO^3) + HO.$$

A golden-yellow, heavy powder remains undissolved, consisting of small cubes which exhibit a perfect metallic lustre, even after pressure with the burnishing steel on paper. When diffused in a state of fine powder through water, it transmits light of a green colour. (According to Laurent, it yields a blue powder.) It may be ignited in a close vessel without fusion or decomposition. (Wöhler.)

	Calculation.		Or:			Malaguti.	Wöhler.
NaO....	31·2	8·14	Na........	23·2	6·05	6·03	6·60
WO^2....	112·0	29·23	$3W$	288·0	75·16	74·33	73·89
$2WO^3$	240·0	62·63	$9O$........	72·0	18·79	19·64	
	383·2	100·00		383·2	100·00	100·00	

When ignited in the air, it assumes a steel-grey colour on the surface, fuses gradually (the change proceeding from the surface to the interior), and yields a transparent mass of [ter?] tungstate of soda, which, on cooling, forms an opaque white mass, and protects the inner portions of the double salt from oxidation. It behaves in a similar manner in oxygen gas, exhibiting, however, a feeble combustion. It is decomposed by chlorine at a red heat, with feeble emission of light, the products being [tungstate of] chloride of tungsten which sublimes, and a mixture of chloride of sodium with a large quantity of tungstic acid, coloured green by tungstic oxide. By fusion with sulphur it is completely resolved into sulpho-tungstite of sodium. (p. 42.) (Wöhler.) 100 parts of the double salt fused with sulphur in a close vessel, yield 112·66 parts of sulphide of tungsten and sodium. (Malaguti.) $2(NaO,WO^3 + WO^2, WO^3) + 23S = 2(NaS, 3WS^3) + 9SO^2$; hence, from one atom of $(NaO,WO^3 + WO^2,WO^3)$ there results one atom of $NaS,3WS^3$; the former weighs 383·2, the latter 423·2; now 383·2 : 423.2 = 100 : 110·44, a number which accords with the result of Malaguti's experiment. The double salt is decomposed and dissolved by hydrofluoric acid, but not by other acids—not even by boiling aqua-regia;—it is likewise unaffected by solutions of the alkalis. (Wöhler.)

E. Fluoride of Tungsten and Sodium with Tungstate of Soda.—$NaF,WF^3 + NaO,WO^3$. Crystallizes less distinctly and dissolves more readily in water than the corresponding potassium compound. (Berzelius.)

OTHER COMPOUNDS OF TUNGSTEN.

With manganese, antimony, bismuth, tin, lead, iron, copper, and silver; but not with gold or platinum. These alloys have a brown colour and are generally brittle.

CHAPTER XIX.

MOLYBDENUM.

Scheele. *Opusc.* 1, 200.
Ilsemann. *Crell. Ann.* 1787, 1, 407.
Heyer. *Crell. Ann.* 1787, 2, 21, and 124.
Hjelm. *Crell. Ann.* 1790, 1, 39;—1791, 1, 179, 248, 266, 353 and 429; 2, 59;—1792, 1, 260; 2, 358;—1794, 1, 238.
Richter. *Ueber die neuern Gegenstände der Chemie.* 1, 49; 2, 97; 10, 86.
Hatchett. *Phil. Transact.* 1795, 323; also *Crell. Ann.* 1797, 1, 314, 417 and 498.
Bucholz. *Scher. J.* 9, 485.—Also *A. Gehl.* 4, 598.
Brandes. *Schw.* 29, 325, and 331.
Berzelius. *Schw.* 22, 51.—*Ann. Chim. Phys.* 17, 5.—*Pogg.* 4,153. *Pogg.* 6, 331 and 369.—*Pogg.* 7, 261.
Svanberg & Struve, *Abhandlungen der Konigl. Acad. in Stockholm*, 1848. Also *J. pr. Chem.* 44, 257.

Wasserblei, Molybdän, Molybdänum, Molybdène.

History. Scheele in 1778 discovered molybdic acid in a mineral hitherto confounded with graphite; Hjelm in 1782 prepared the metal from molybdic acid. Berzelius described most of its chemical characters and combinations.

Sources. In small quantity only as molybdic acid (*molybdic ochre*); as sulphide of molybdenum (*Wasserblei*); and as molybdate of lead (*Gelb-bleierz*). The pig-iron, obtained in smelting the Mansfeld copper-ore, contains from 9 to 28 per cent. of molybdenum. (Heine, *J. pr. Chem.* 9, 204.)

Preparation.—1. By exposing either of the oxides of molybdenum, or molybdate of ammonia, or the acid molybdate of potash to a full white heat in a charcoal crucible. The reduction is easily effected, and may even be performed before the blowpipe on charcoal with carbonate of soda; but to obtain a fused button of metal, a very strong heat is required. (Berzelius.)—2. Hydrogen gas dried by means of chloride of calcium, is passed over molybdic acid heated to whiteness in a porcelain tube, till no more water is produced; the apparatus is then allowed to cool, the current of hydrogen being kept up without intermission. (Berzelius.)—3. By exposing molybdic acid to the oxy-hydrogen blowpipe-flame (Clarke);—or 4. By introducing it into the circuit of Children's voltaic battery (Children).

Properties. The metal, as prepared by the first method, is silver-white, with a strong metallic lustre, and has a specific gravity of 7·5 (Hjelm), 8·62 (Bucholz); when in small pieces it may be beaten out flat without breaking; it scratches an alloy of 3 parts silver and 1 part copper. Fuses but imperfectly in the most powerful blast-furnaces, so that it has only been obtained in small masses. (Bucholz.)—The molybdenum prepared by the second method is an ash-grey powder, which remains unaltered in the air; assumes metallic lustre by pressure; and conducts electricity. (Berzelius.) That obtained by the third method is silver-white; that obtained by the fourth, steel-grey.

Compounds of Molybdenum.

MOLYBDENUM AND OXYGEN.

Molybdenum loses its metallic lustre by exposure to the air for some days at ordinary temperatures; when heated in the air, it becomes first brown, then blue, and lastly white; and—if the temperature is sufficiently high—emits light, gives off fumes, and is converted into crystallized molybdic acid. (Berzelius.)—On charcoal in the inner blowpipe-flame, molybdenum is not altered; but in the outer flame it covers the charcoal for a small space around, partly with transparent, brilliant, crystalline scales, partly with powder of molybdic acid, which is yellow while hot and becomes white on cooling. This coating may indeed be driven to a greater distance by the action of the outer flame, but it leaves on the former spot a portion of dark copper-coloured oxide of molybdenum. (Plattner.)—When heated with nitre, molybdenum is rapidly oxidized; with hydrate of potash, the action is slow, and attended with evolution of hydrogen gas. (Berzelius.)—It decomposes aqueous vapour at a red heat, first forming the blue oxide, and then molybdic acid. (Regnault.)—It dissolves in nitric acid with evolution of nitrous fumes, and in hot oil of vitriol with evolution of sulphurous acid. If the acids are used in small quantity only, the metal is converted into molybdic oxide; with a larger proportion of oil of vitriol, the blue oxide is formed; and with a larger proportion of nitric acid, the product is molybdic acid, which is also partially deposited in the solid state. A mixture of nitric acid with sulphuric or hydrochloric acid rapidly oxidizes and dissolves the metal. An aqueous solution of chlorine likewise oxidizes and dissolves molybdenum. Hydrofluoric acid, hydrochloric acid, dilute sulphuric acid, boiling solution of potash, and water, do not exert any oxidizing power upon it. (Bucholz, Berzelius.)

A. MOLYBDOUS OXIDE, OR PROTOXIDE OF MOLYBDENUM. MoO.

Formation. All the metals which decompose water withdraw from molybdic oxide and molybdic acid, in presence of one of the stronger acids, such a quantity of oxygen that molybdous oxide is produced.

Preparation. Equal weights of mercury and hydrochlorate of molybdic oxide dissolved in water containing free acid, are introduced into a bottle, and liquid amalgam of potassium gradually added drop by drop; as the action ceases, the liquid first becomes greenish, and afterwards black and opaque. As soon as the molybdous oxide begins to separate, and the potassium appears to be oxidized by the water, the solution is decanted from the mercury,—and the black hydrate of molybdous oxide precipitated by ammonia, then washed, dried over oil of vitriol in vacuo, and lastly ignited out of contact of air. If an excess of hydrochloric acid were not present, hydrated bi-oxide of molybdenum would be thrown down before it was converted into the protoxide, and would form a dark brown instead of a black precipitate.—2. A concentrated solution of molybdate of ammonia, potash, or soda, is supersaturated with hydrochloric acid till the precipitated molybdic acid is re-dissolved. The solution is then digested with zinc, by which it is first turned blue, then reddish brown, and lastly black. It is then poured off from the zinc, and mixed with a quantity of ammonia just sufficient to precipitate the protoxide of molybdenum alone. The hydrated protoxide is then collected on a filter; washed, after the original liquid has passed through, with repeated quantities of water containing ammonia, to remove the oxide of zinc which is thrown down with it in small quantities; afterwards washed with pure cold water; and lastly pressed, dried, and ignited as above. Portions of oxide of zinc remain mixed with the molybdous oxide thus obtained.—3. Fused or sublimed molybdic acid digested for a long time with hydrochloric acid and zinc, is wholly converted into anhydrous molybdous oxide, the merest trace only being dissolved. The molybdous oxide thus obtained oxidizes rapidly in the air, probably because the oxygen easily re-enters the pores from which it has been expelled. During the oxidation, the substance first assumes a purple and afterwards a blue colour. (Berzelius.)

Properties. Molybdous oxide prepared by the first and second methods is pitch-black; that obtained by the third method is black, but when exposed to the direct rays of the sun, exhibits a dark brass-yellow colour; it takes the crystalline form of the molybdic acid from which it is prepared.

Calculation,* according to Berzelius.

Mo	48	....	85·71
O	8	....	14·29
MoO	56	....	100·00

MoO = 568·52 + 100 = 698·52. (Berzelius.)

Decompositions. By charcoal, and by potassium.

Combinations.—*a.* With Water.—HYDRATED MOLYBDOUS OXIDE.—Prepared by precipitating the protochloride of molybdenum with ammonia (*vid. sup.*); it may be washed in the open air, but must be dried in vacuo; because, if exposed to the air during the latter operation, it assumes a somewhat lighter colour, from incipient oxidation. It is black. When heated in vacuo, it gradually parts with its water. The remaining anhydrous oxide, when heated nearly to redness, emits a vivid light, which, however, lasts but for a moment. (Berzelius.)

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[*] Svanberg & H. Struve (*J. pr. Chem.* 44, 301) have determined the atomic weight of molybdenum by fusing a given weight of molybdic acid with carbonate of soda, and observing the quantity of carbonic acid expelled. The results of three experiments are 45·848, 46·12, and 45·904. By a different process, however, *viz.*, by igniting a weighed quantity of sulphide of molybdenum in moist, and afterwards in dried air, and observing the increase of weight, the atomic weight was found to be 46·066 or 47·112: (sulphur = 16·06.) But the errors incidental to this process, and indeed to every other yet tried, render the atomic weight of molybdenum still a matter of uncertainty. ¶

b. Anhydrous molybdous oxide is insoluble in acids; the hydrate difficultly soluble. The MOLYBDOUS SALTS in the solid state are dark grey or black; their aqueous solutions are black, or purple (especially if they contain excess of acid), and nearly opaque; when largely diluted, however, they are transparent and of a greenish brown colour. Their taste is purely astringent, not metallic. They oxidize less rapidly in the air than the molybdic salts: consequently their aqueous solutions can be more easily evaporated without alteration. Hydrosulphuric acid precipitates from them brownish black sulphide of molybdenum, but not till after some time. The caustic alkalis and their carbonates throw down the black hydrated protoxide, which redissolves in excess of carbonate of ammonia, and sparingly in excess of carbonate of potash or soda. Phosphate of soda precipitates brownish black molybdous phosphate. Hydrosulphate of ammonia precipitates yellowish brown sulphide of molybdenum, soluble in excess of the ammoniacal salt. If oxide of zinc is present, it remains undissolved in the form of sulphide of zinc. Ferrocyanide of potassium produces a dark brown precipitate, which dissolves in an excess of the reagent, forming a dark brown solution. Ferricyanide of potassium produces a reddish brown precipitate. Oxalic acid does not affect molybdous salts.

¶ *Sesquioxide of Molybdenum.* Prepared, according to Kobell (*J. pr. Chem.* 41, 158; *Pharm. Centr.* 1847, 678), by boiling copper in a solution of molybdic acid. ¶

B. MOLYBDIC OXIDE OR BI-OXIDE OF MOLYBDENUM. MoO^2.

Brown or *Violet-brown Oxide of Molybdenum* of Bucholz.

Formation and *Preparation.*—1. By gently heating molybdenum for a short time in contact with the air. (Bucholz.)—2. Molybdous oxide takes fire when heated in the air, burning with feeble glow, if free from oxide of zinc, and is converted into molybdic oxide. (Berzelius.)—3. By strongly igniting molybdate of ammonia in a covered crucible. (Bucholz.)—The oxide obtained by this latter method is contaminated with molybdic acid, which gives it a lighter colour; it may, however, be removed by solution of potash or hydrofluoric acid. (Berzelius.)—4. Roasted sulphide of molybdenum is dissolved in aqueous solution of carbonate of soda; the mixture evaporated to a small bulk; the solution filtered from the insoluble portions, and evaporated to dryness; the residue ignited; the resulting colourless salt dissolved in water, which takes up foreign matters at the same time; the solution again filtered, and evaporated to dryness; the residue reduced to powder, and intimately mixed with half its weight of sal-ammoniac; the mixture ignited in a closely covered crucible till the sal-ammoniac is entirely expelled; the chloride of sodium dissolved out by water, and the molybdic acid by a boiling dilute solution of caustic potash; and lastly, the molybdic oxide thrown on a filter, washed with water, and dried. (Berzelius.)

Properties. Molybdic oxide, as prepared by the fourth method, is brownish black while moist; dark brown when dry; and of a brilliant purple colour in direct sunshine (Berzelius); the third method yields it in dark, copper-coloured, crystalline scales, having the metallic lustre, and of specific gravity 5·666. (Bucholz.)

	Calculation.		Berzelius.	Bucholz.
MO	48	75	75	73
2O	16	25	25	27
MoO^2	64	100	100	100

($MoO^2 = 598{\cdot}52 + 200 = 798{\cdot}52$. Berzelius.)

Decompositions.—Reduced to the metallic state by charcoal and potassium. According to Berzelius, it remains unaltered after ignition in an atmosphere of dry chlorine gas.

Combinations.—*a.* With Water.—*α.* HYDRATED MOLYBDIC OXIDE of Bucholz.—1. An aqueous solution of bichloride of molybdenum is precipitated by ammonia.—2. A concentrated solution of molybdic acid in hydrochloric acid is digested with finely divided molybdenum till the liquid, which first assumes a blue colour, becomes dark red; the oxide is then precipitated by ammonia.—3. Molybdic acid is digested with hydrochloric acid and copper, till it is entirely dissolved; and the resulting hydrochloric acid solution of molybdic oxide and oxide of copper is mixed with a large excess of ammonia, by which the oxide of copper is redissolved. The molybdic oxide is then washed with water containing ammonia. The precipitate should be washed on the filter, first with solution of sal-ammoniac, and afterwards with alcohol, the solvent action of which is much less than that of pure water. The oxide is then pressed out and dried in vacuo over oil of vitriol, to prevent oxidation.

The hydrated oxide is reddish brown when recently precipitated, but blackish brown after drying. When ignited in vacuo, it leaves the anhydrous brown oxide. By exposure to the air it becomes darker, from formation of blue oxide, and acquires a certain degree of lustre. From this substance water dissolves out the blue oxide, together with portions of the brown oxide, forming a green solution and leaving hydrated molybdic oxide in a state of greater purity. (Berzelius.)

β. SOLUTION OF MOLYBDIC OXIDE.—The hydrate dissolves slowly and in small quantity only, in pure water. The solution is yellow, or when fully saturated, dark red; reddens litmus; has a slightly rough and afterwards somewhat metallic taste; and deposits the hydrate on the addition of sal-ammoniac or some other salt. When kept for several weeks in a stoppered bottle, it becomes gelatinous, but does not lose its transparency. When spontaneously evaporated in the air, it first gelatinizes, and then dries up to a brownish black hydrate which is no longer soluble in water, but yields up the blue oxide which has been produced from it. (Berzelius.)

b. With Acids forming the MOLYBDIC SALTS.—The bi-oxide, after ignition, is insoluble in all aqueous acids, traces only being dissolved by boiling oil of vitriol and by a boiling solution of cream of tartar; after which no more is taken up, even if the oxide be digested in fresh acid. It dissolves but slowly in fused bisulphate of potash or soda. The molybdic salts are therefore prepared either by dissolving the hydrated oxide in acids, or by digesting an excess of molybdenum in the acid in which it is to be dissolved, and adding dilute nitric acid, drop by drop (excepting when a nitrate is to be formed), till the other acid is saturated with molybdic oxide; or by digesting an excess of molybdenum with molybdic acid and the acid which is required to dissolve the oxide when formed,—hydrochloric acid, for example,—till the blue colour first produced is converted into a reddish brown; or lastly, by digesting molybdic acid with copper and hydrochloric acid, which, in that case, dissolves oxide of copper and molybdic oxide together. The salts of molybdic oxide, in the anhydrous state, are almost black; but when hydrated, they are red, and yield reddish brown solutions with water. They have a rough, somewhat acid, and subsequently metallic taste. Their aqueous solutions, when heated in the air, have a tendency to become blue by oxidation. With zinc they first blacken, and then yield a black precipitate of hydrated molybdous oxide. Hydrosulphuric acid gives a precipitate of brown sulphide of molybdenum, but not till after some time. With ammonia or potash, they yield a rusty brown precipitate, insoluble in excess of the alkali. If the quantity of ammonia added is insufficient for saturation, the precipitate re-dissolves in the liquid, and if the solution is very dilute, it does not appear till after the addition of sal-ammoniac, by which the solubility of the hydrated oxide in water is destroyed. The carbonates of potash and soda produce the same precipitate, which, however, is soluble in excess of the reagent. Phosphate of soda gives a brownish white precipitate. Hydrosulphate of ammonia throws down yellowish brown sulphide of molybdenum, soluble in excess of the ammoniacal salt. Ferrocyanide or ferricyanide of potassium gives a dark brown precipitate, insoluble in excess of the precipitant. Tincture of galls imparts to salts of molybdic oxide a deep reddish brown colour, at the same time producing a scanty greyish brown precipitate. Oxalic acid causes no precipitation. The insoluble molybdic salts are rapidly decomposed in the air, when covered with solution of caustic potash or soda, an alkaline molybdate being formed. (Berzelius.)

Between the above described brown oxide and molybdic acid, the olive green oxide and the blue oxide must be interposed according to their proportions of oxygen: these compounds, however, should perhaps be regarded not as distinct oxides, but as compounds of the brown oxide with different quantities of molybdic acid.

Olive-green Oxide.

1. If 2 parts of powdered molybdenum are digested in a stoppered bottle, at a temperature between 40° and 60°, with one part of molybdic acid and a very large quantity of water, a liquid is obtained after some days, which at first appears dark blue, then dark green, and afterwards undergoes no further change. From this solution, powdered sal-ammoniac completely precipitates the green oxide, which, however, redissolves in pure water.—2. When a mixture of the brown and blue oxides of molybdenum is dissolved in hydrochloric acid, ammonia throws down from the solution a similar green precipitate, which may be washed with water containing sal-ammoniac, but from which pure water dissolves out the blue oxide, leaving the brown oxide in the state of hydrate. (Berzelius.) This oxide, according to Berzelius, is identical with the *light blue oxide* which Bucholz obtained by digesting the blue oxide with finely divided molybdenum and water.

Blue Oxide; Bucholz's *Molybdenous acid.*

Formation and *Preparation.*—1. Molybdenum, the protoxide, or the brown oxide is heated in the air, but not for a very long time.—2. Molybdenum, or hydrated molybdic oxide, is moistened with water and exposed to the air for a considerable time, or boiled with water in an open vessel.—3. A mixture of 4 parts of molybdic acid with 2 parts of molybdenum, or with 3 parts of the brown oxide, is reduced to a fine paste with a small quantity of water, a gentle heat being applied. The mixture is then boiled with water; the clear liquid poured off; and the insoluble portion again rubbed up in a mortar and boiled with a fresh quantity of water. The blue solutions thus obtained are then evaporated out of contact of air, or in contact with molybdenum. (Bucholz.)—4. An aqueous solution of bimolybdate of ammonia is mixed with a solution of bichloride of molybdenum—whereupon the liquid immediately becomes blue and deposits the blue oxide; this is collected on a filter. If the bimolybdate of ammonia be added in excess, the solution which passes through the filter is of a light-blue colour; but if the bichloride of molybdenum predominates, the filtrate is green. The hydrated oxide on the filter is washed, first with water containing sal-ammoniac, which acquires but a slight colour, and then with alcohol or cold water, which, however, dissolve it in larger quantity; it is lastly dried in the air, as it is not liable to become oxidized. (Berzelius.)

The hydrated oxide prepared by either of the above methods may be rendered anhydrous by ignition in vacuo. (Berzelius.)

The oxide is nearly black after ignition. (Berzelius.)

As the blue oxide is produced by the double decomposition of bimolybdate of ammonia and bichloride of molybdenum, it must be a compound of 1 atom (18 per cent.) of molybdic oxide, and 4 atoms (82 per cent.) of molybdic acid.

$$2(NH^3, 2MoO^3) + MoO^2, 2HCl = 2(NH^3, HCl) + MoO^2, 4MoO^3.$$

In fact, the analysis by ammonia gives this proportion.. (Berzelius.)

Decompositions. Ammonia or potash dissolves out molybdic acid from the hydrate, and leaves molybdic oxide (a very dilute alkaline solution dissolves the whole compound and does not deposit the molybdic oxide till it is boiled); hence molybdenous acid does not form salts. The stronger acids act in a similar manner on the ignited oxide. (Berzelius.)

Combinations.—a. With Water.

α. Hydrate of the Blue Oxide.—Prepared by either of the four methods given above. Dark blue powder, resembling powdered indigo, having a bitter, rough, metallic taste, and reddening litmus strongly. (Bucholz.)

β. Solution of the Blue Oxide.—The ignited oxide imparts to water only a slight blue colour. The hydrate dissolves very abundantly in water, especially in hot water, and nothing is deposited on cooling. From the intensely dark blue solution, which, when highly concentrated, is of a syrupy thickness (Bucholz), sal-ammoniac precipitates nearly all the hydrate, though the supernatant liquid still retains a light blue colour. When evaporated in the air, it becomes lighter coloured from oxidation. (Berzelius.)

b. With Acids, forming salts whose base is a compound of molybdic acid and molybdic oxide. Acids form with the blue oxide dark blue solutions, which, when evaporated, yield dark blue masses of the consistence of syrup or extract, and on exposure to the air, lose their colour by oxidation, especially when heated. Potash decolorizes the blue solution, and precipitates hydrated brown oxide; when largely diluted, however, the liquid remains blue; sal-ammoniac precipitates some of these solutions only. (Bucholz, Berzelius.)

c. The blue oxide is sparingly soluble in alcohol.

C. Molybdic Acid. MoO^3.

Found native as *Molybdic Ochre.*

Formation.—1. By exposing molybdenum, or its lower oxides, or sulphide of molybdenum, to long continued heat in the air.—2. By the action of nitre on the same substances.—3. By igniting the metal or its oxides in an atmosphere of aqueous vapour. (Regnault, *Ann. Chim. Phys.* 62, 356), or with hydrate of potash (Liebig, *Kastn. Arch.* 2, 57), in which case, hydrogen gas is likewise evolved.

Preparation.—1. Molybdenum or one of its lower oxides is dissolved in excess of nitric acid, and (*a*) the solution either evaporated to dryness, and the residue ignited; or (*b*) left to evaporate spontaneously, and the molybdic acid—which in this case is deposited as a white powder—collected on a filter, purified with water, and dried. (Berzelius.)—2. Sulphide of molybdenum is digested with nitric acid till it loses its grey colour; the mixture is then evaporated, and the molybdic acid produced is freed from the adhering nitric and sulphuric acids by washing with water. (Scheele.)—3. Finely divided, pure native sulphide of molybdenum is roasted—at a strong heat at first, but afterwards at a lower temperature—till it appears yellow while hot and white on cooling.—4. From impure sulphide of molybdenum mixed with quartz, &c., it is necessary first to prepare molybdate of ammonia. (*q. v.*) The salt is then heated for a long time in an open crucible, at a temperature low enough to prevent fusion. (Berzelius.) The molybdate of ammonia prepared from the native molybdate of lead may likewise be used for this purpose. (Wittstein.)

Properties.—As prepared according to (1, *b.*) White, bulky, porous mass, diffusing itself in water in small, silky, crystalline scales: after ignition, by which it loses nothing but 2 per cent. of pure water, it appears white and soft like talc; after fusion, it forms greyish or yellowish white radiated masses; or, after sublimation, brilliant, colourless, transparent laminæ or needles. Its specific gravity is 3·46. (Bergman.) It assumes a lemon-yellow colour every time it is heated. Fuses at a red heat (and more readily when it contains alkali) to a brownish yellow liquid; in covered vessels it volatilizes at high temperatures only, but when exposed to the air, even at its melting point, it volatilizes in white fumes, which condense above the fused acid in the form of a crystalline sublimate. Has a sharp metallic taste, and reddens litmus. Volatilizes when exposed on platinum wire to the blue flame of the blowpipe, imparting to it a yellowish-green tinge. (Plattner.) In the inner flame, it first becomes blue and then brown; if heated on charcoal it fuses and is absorbed; but is reduced by a powerful blast to finely divided metal which sinks in the pores of the charcoal; it may be separated by washing away the lighter particles with water. (Berzelius.)

	Calculation.		Berzelius.	Bucholz.	
MO	48	66·7	66·613	67 to	68
3O	24	33·3	33·387	33 ,,	32
MoO^3	72	100·0	100·000	100	100

($MoO^3 = 598{\cdot}52 + 3.\quad 100 = 898{\cdot}52$. Berzelius.)

Decompositions.—1. Reduced to the metallic state by ignition with potassium or sodium (with vivid incandescence), or with charcoal; in a current of hydrogen gas; in the oxy-hydrogen blowpipe flame; and by a powerful current of galvanic electricity.—2. To molybdous oxide: by digestion with hydrochloric acid and amalgam of potassium, zinc, or other metal capable of decomposing water.—3. To the state of brown oxide: by ignition in combination with ammonia, or by digestion with hydrochloric acid and molybdenum or copper.—4. To the state of blue oxide: by a small quantity of hydrosulphuric acid in presence of water or on exposure to heat, the action being attended with separation of sulphur; by sulphurous acid, with production of sulphuric acid; by aqueous hydriodic acid, with separation of free iodine, and formation of a liquid which is green at first, but afterwards becomes blue; by boiling hydrochloric acid, with disengagement of chlorine; by nitric oxide in presence of water, with formation of nitrous acid (Kastner, *Kastn. Arch.* 26, 465); by protochloride of tin, with formation of bi-oxide of tin; by digestion with water and with metallic molybdenum.—5. To sulphide of molybdenum: by hydrosulphuric acid in excess, in presence of water, or when aided by heat. Molybdic acid is not affected by fusion with metallic molybdenum. (Berzelius.)

Combinations.—*a.* With Water.—AQUEOUS MOLYBDIC ACID.—Molybdic acid dissolves, according to Bucholz, in 500 parts of cold water, and in a much smaller quantity at a higher temperature: according to Hatchett, it requires 960 parts of hot water. The solution yields a red precipitate with ferrocyanide of potassium, but not till one of the stronger acids is added.

b. With the stronger acids. The affinity of molybdic acid for other acids is very feeble. After ignition, it is but slightly soluble in a boiling aqueous solution of cream of tartar; before ignition, however, it dissolves in some of the other acids. The solutions thus obtained are sometimes colourless, sometimes yellow or brownish. By metallic zinc or tin, they are first turned blue, then green, and lastly black, molybdous oxide being precipitated; by digestion with copper, they become dark red. Protochloride of tin produces a greenish-blue precipitate, which dissolves in hydrochloric acid, forming a green solution. Hydrosulphuric acid in small quantity colours them blue; in larger quantities it produces a blackish brown precipitate (a mixture of bisulphide of molybdenum with sulphur: *Berzelius*). The supernatant liquid is green, and deposits after long standing, or more rapidly when heated, a further quantity of brown sulphide of molybdenum; a small quantity of molybdenum, however, still remains in the solution. If the liquid contains but a very small quantity of molybdic acid, it forms with excess of sulphuretted hydrogen, a green solution, which deposits brown sulphide of molybdenum only after long standing or when heated. Hydrosulphate of ammonia behaves in a similar manner to hydrosulphuric acid. (Bucholz, Berzelius.) Ferrocyanide of potassium produces a dense, reddish-brown precipitate, soluble in excess of the reagent and also in ammonia. (Berzelius.) Ferrocyanide of potassium gives a somewhat lighter coloured precipitate, which is likewise soluble in ammonia. (H. Rose.) Tincture of galls throws down a green precipitate. (Smithson.)

c. With Salifiable Bases, forming the SALTS OF MOLYBDIC ACID, MOLYBDATES. Molybdic acid expels carbonic acid from solutions of the alkaline carbonates. It chiefly forms salts containing one or two atoms of acid. The salts are generally colourless or yellow; when soluble, they have a faint metallic taste. They are fixed in the fire, unless the base is volatile. The addition of a very small portion of concentrated sulphuric, hydrochloric, or nitric acid to a salt of molybdic acid mixed with a small quantity of water, causes the separation of white, curdy molybdic acid, which is soluble in a slight excess of either of the three acids, or in a large quantity of water; phosphoric acid and oxalic acid do not produce this effect. ¶ According to Svanberg & Struve, when phosphoric acid or a liquid containing it is added to a solution of an alkaline molybdate, together with an excess of hydrochloric acid, the mixture turns yellow, and after some time deposits a yellow precipitate. (Gmelin has likewise observed this effect in the case of molybdate of ammonia.) This reaction is stated to be so delicate, that it may be employed for the detection of phosphoric acid. (*J. pr. Chem.* 44, 257.) ¶ The molybdates, when supersaturated with a stronger acid, yield, according to Berzelius, the same results as those just described under *b*. The molybdates (molybdate of ammonia, but not the potash salt: *Gmelin*), heated with oil of vitriol, form a blue mass, either immediately or after cooling. (Smithson.) When heated on charcoal in the inner blowpipe flame with carbonate of soda, these salts yield metallic molybdenum, or an alloy of molybdenum with the metal existing in the base. With borax and microcosmic salt, they give a brown colour in the inner flame. The compounds of molybdic acid with the fixed alkalis, when mixed with sal-ammoniac and ignited, yield molybdic oxide, together with chloride of the alkali-metal, which latter may be extracted by water. (Berzelius.) The alkaline molybdates in solution, give, with a small quantity of protochloride of tin, a blue colour; with a larger quantity, a dingy blue precipitate which dissolves in oil of vitriol, producing a splendid blue solution; with a still larger proportion of the tin-salt, the precipitate is of a dull green colour, and yields with oil of vitriol, a beautiful green solution. The molybdates of ammonia, potash, and soda, are the only salts of molybdic acid that dissolve readily in water; of the rest, some dissolve with difficulty, and others are completely insoluble. The aqueous solutions of the more soluble alkaline molybdates are coloured yellow by hydrosulphuric acid, from formation of a double sulphide of molybdenum and the alkali-metal, [MS,MoS^3] and then yield with acids a brown precipitate of tersulphide of molybdenum. They give white precipitates with the salts of the earthy alkalis and of the earths, and precipitates of various colours with those of the heavy metals: *e. g.* white, with salts of lead or silver; yellow with ferric salts; and yellowish white with mercurous salts. (Berzelius.) With tincture of galls they give, according to Smithson, a reddish yellow precipitate which turns green on the addition of an acid. [The mixture is dark reddish brown but transparent; the addition of a drop of hydrochloric acid causes the separation of a dense, dingy brown precipitate, which, by a larger quantity of acid, is converted into small reddish brown flakes.]

None of the oxides of molybdenum combine with carbonic acid. (Berzelius.)

MOLYBDENUM AND BORON.

A. BORATE OF MOLYBDOUS OXIDE.—Dark grey precipitate, which turns black on drying, is insoluble in water, and dissolves but sparingly in aqueous solution of boracic acid. (Berzelius.)

B. BORATE OF MOLYBDIC OXIDE.—*a.* Bichloride of molybdenum gives with borate of ammonia a rusty-yellow precipitate, insoluble in water.—*b.* Hydrated molybdic oxide dissolves in boiling boracic acid, yielding a yellow solution which, when evaporated, solidifies to a jelly, and deposits the neutral salt. (Berzelius.)

C. BORATE OF MOLYBDIC ACID.—An aqueous solution of boracic acid dissolves molybdic acid on boiling, and when the latter is in excess, forms with it an opaque viscid liquid of the consistence of turpentine. The solution becomes milky as it cools, and yields a colourless filtrate which on evaporation deposits colourless crystals, decomposable by alcohol into a yellow powder and boracic acid (containing a very small quantity of molybdic acid, which dissolves in the menstruum). (Berzelius.)

MOLYBDENUM AND PHOSPHORUS.

A. PHOSPHIDE OF MOLYBDENUM.—Prepared by Pelletier, but not further examined.

B. PHOSPHATE OF MOLYBDOUS OXIDE.—*a. Diphosphate.* Formed when protochloride of molybdenum is precipitated by ordinary diphosphate of soda. Dark grey precipitate, soluble in excess of protochloride of molybdenum.

b. Acid Phosphate.—The solution of the hydrated protoxide in aqueous phosphoric acid yields on evaporation a dark purple, syrupy mass, which is deliquescent and dissolves in ammonia, forming a blackish brown solution. (Berzelius.)

C. PHOSPHATE OF MOLYBDIC OXIDE.—*a. Monophosphate.*—Ordinary diphosphate of ammonia, added to a solution of the bichloride of molybdenum, throws down light red flakes, while the liquid itself remains yellow in consequence of a portion of the salt being dissolved.

b. Acid phosphate.—A saturated solution of hydrated molybdic oxide in aqueous phosphoric acid, dries up by spontaneous evaporation to a transparent, red, tenacious, uncrystallizable mass, which dissolves in ammonia with a red colour, but separates again almost entirely in the course of an hour. (Berzelius.)—Bucholz obtained a similar compound by heating a mixture of molybdenum and phosphoric acid for a long time, the heat being raised to redness toward the end of the process: it forms a greyish-blue mass having a very acid and subsequently metallic, astringent taste. It dissolves in water, forming a yellowish-brown solution.

D. PHOSPHATE OF MOLYBDIC ACID.—*a. Basic Phosphate.*—Molybdic acid, digested while still moist with a small quantity of aqueous phosphoric acid, yields a lemon-yellow salt insoluble in water. (Berzelius.) [For the action of phosphoric acid on molybdic acid in combination, *vid.* p. 57.]

b. Acid Phosphate.—With a larger proportion of aqueous phosphoric acid, the salt *a*, which is first produced, dissolves on the application of heat, and forms a colourless liquid, which yields, on evaporation, a tenacious, uncrystallizable, transparent mass, having a very rough taste, and readily soluble in water and alcohol. The alcoholic solution is yellow, but turns blue on evaporation, and leaves a brown opaque residue, which again dissolves in water, forming a blue solution. (Berzelius.)

MOLYBDENUM AND SULPHUR.

A. BISULPHIDE OF MOLYBDENUM.—*Molybdous Sulphide, Sulpho-molybdous Acid.*—Found native as *Wasserblei* or *Molybdenum-glance.* The residue obtained when the higher sulphides of molybdenum are heated. Likewise produced by igniting molybdic acid with sulphur. The native variety belongs to the hexagonal system of crystallization (B, *a.* I, 16); *Fig.* 135 and 138. Cleavage distinct parallel to *p.* Sp. gr. = 4·6. Softer than calcspar. Soft and unctuous to the touch. Bluish grey, with metallic lustre. Leaves a greenish streak on porcelain. The artificial compound is a black shining powder.

	Wasserblei.		Bucholz.	Brandes.	Seybert.
Mo	48	60	60	59·6	59·42
2S	32	40	40	40·4	39·68
MoS^2	80	100	100	100·0	99·10

In close vessels it sustains a high temperature without fusing or undergoing any change, and, according to H. Rose, is not decomposed by ignition in dry hydrogen gas. When heated in the air it is converted into molybdic acid, with evolution of sulphurous acid.

Before the blowpipe on charcoal it gives off sulphurous acid, covering the charcoal with a yellowish-white incrustation; but it burns with great difficulty, and the combustion is but imperfect. (Berzelius.) On platinum wire it colours the outer blowpipe flame green. (Kobell.) It colours a bead of borax mixed with nitre, dark-brown in the inner flame, and light-brown in the outer.

It decomposes vapour of water at a red heat slightly, but at a higher temperature with greater facility. (Regnault.) Detonates with nitre, forming molybdate of potash. Dissolves readily in warm aqua-regia, producing molybdic and sulphuric acid. Easily oxidized by nitric acid. Dissolves in boiling oil of vitriol with evolution of sulphurous acid, and forms a blue solution. (Berzelius.) [For its behaviour with oxide of lead at a red heat, *vid.* Berthier, *Ann. Chim. Phys.* 39, 251.]

TERSULPHIDE OF MOLYBDENUM.—*Molybdic Sulphide, Sulpho-molybdic acid.*—Formed by the decomposition of molybdic acid by hydrosulphuric acid.—1. A concentrated solution of a salt of molybdic acid is saturated with hydrosulphuric acid; a stronger acid added in excess; and the precipitate digested with it for some time, in order to decompose any alkaline hydrosulphate possibly thrown down with it, and then purified with water: the water however redissolves a small portion.—2. The solution of molybdic acid in an alkaline bihydrosulphate (MS,HS) is precipitated by a stronger acid.—The sulphide of molybdenum thus obtained is likely to be mixed with sulphur or molybdic acid. In the moist state, it appears reddish brown, but when dried it forms a blackish brown powder, which also leaves a blackish brown streak on porcelain or paper. (Berzelius.)

	Calculation.		Berzelius.
Mo	48	50	49·72
3S	48	50	50·28
MoS^3	96	100	100·00

When heated in a close vessel it loses the third atom of sulphur, and is converted into bisulphide of molybdenum, having a powerful metallic lustre. Exposed to the air in a moist state, it forms a small quantity of sulphuric acid, which disintegrates the filter-paper. It dissolves with difficulty—except when boiled—in a concentrated solution of potash, and is partially decomposed into KS, MoS^4. It is somewhat soluble in water, especially in hot water, yielding a dark-yellow solution. (Berzelius.)—The liquid may likewise be regarded as containing MoO^3, 3HS.

Tersulphide of molybdenum unites with the more basic metallic sulphides, forming *Sulpho-molybdates*, or *Molybdo-sulphites*. For one atom of the basic sulphide they contain from 1 to 3 atoms of tersulphide of molybdenum.—*a.* The compounds of this nature which are soluble in water are obtained: 1. By passing hydrosulphuric acid through a concentrated solution of a salt of molybdic acid, and evaporating. If the solution is dilute, the absorption takes place more slowly. $KO,MoO^3 + 4HS = KS,MoS^3 + 4HO$. The liquid assumes a yellowish red, or, when iron is present, a reddish-brown colour.—2. By dissolving tersulphide of molybdenum in an aqueous solution of a metallic sulphide (or alkaline hydrosulphate). If an alkaline bihydrosulphate is used, the act of solution is attended with disengagement of hydrosulphuric acid, and takes place but slowly, unless heat is applied. By boiling bisulphide of molybdenum and sulphur in the aqueous solution of an alkali, especially a solution of baryta, strontia, or lime, an alkaline bisulphide is first formed, and then a compound of a protosulphide of the alkali-metal with tersulphide of molybdenum.—*b.* The insoluble compounds are prepared by precipitating the soluble compounds with salts of the earths and of the heavy metals.

The compounds soluble in water are crystallizable, and in that state often appear green by reflected, and red by transmitted light; the rest have a fine red colour; but an excess of sulphide of molybdenum makes them darker, and the presence of iron renders them brown.

The sulpho-molybdates are either wholly or for the most part decomposed when ignited out of contact of air; the basic metallic sulphide either combining with the third atom of sulphur in the sulphide of molybdenum, when capable of so doing, and producing a mixture of bisulphide of molybdenum and another metallic bisulphide removable by water (as with potassium or sodium, in which case, however, the decomposition of the compound, even at a strong red heat, is but imperfectly effected): or the third atom of sulphur escapes in the form of vapour, and leaves a mixture of bisulphide of molybdenum with the other metallic protosulphide.

Only the compounds of tersulphide of molybdenum with the sulphides of the alkali-metals and of magnesium, are soluble in water. The solutions are red, inclining to brown if the sulphide of molybdenum is in excess; but reddish yellow if the other metallic sulphide predominates. (These solutions may also be supposed to contain a double hydrosulphate; for example, in the potassium compound, by the decomposition of 4 atoms of water: $KO, HS + MoO^3, 3HS$.) If the solutions are boiled for some time in close vessels, they deposit—especially when the tersulphide of molybdenum is in excess—bisulphide of molybdenum, and a compound of the basic sulphide (or sulphur-base), with tetrasulphide of molybdenum: hydrosulphuric acid is evolved at the same time. The solutions of these compounds remain tolerably stable in the air, provided they are concentrated, and contain more than one atom of tersulphide of molybdenum to one atom of the sulphur-base. But if the sulphide of the alkali-metal (or alkaline hydrosulphate) predominates, or if free alkali is present, or if the solution itself is dilute, it gradually becomes darker, from formation of an alkaline hyposulphite and a compound of the sulphur-base with excess of tersulphide of molybdenum. The latter substance is then decomposed, though very slowly, with separation of tersulphide of molybdenum; and the supernatant liquid which is blue, contains alkali, partly in combination with acids of sulphur, partly with molybdic acid and blue oxide of molybdenum. Acids added to these aqueous solutions precipitate tersulphide of molybdenum, and liberate sulphuretted hydrogen. Metallic oxides which readily part with their oxygen, produce in these solutions a molybdate of the alkali and a new metallic sulphide, which enters into combination with the undecomposed portion of the tersulphide of molybdenum. (Berzelius.)

C. TETRASULPHIDE OF MOLYBDENUM.—*Per-sulphomolybdic Acid, Persulphide of Molybdenum* of Berzelius.—Bimolybdate of potash is saturated with hydrosulphuric acid, and the nearly black liquid—which contains KS, MoS^3 in solution, and a compound of KS with excess of MoS^3 diffused through it—is boiled in a retort for some hours—whereby hydrosulphuric acid is expelled and the precipitate increased. The solution when cold is filtered, and the black powder of bisulphide of molybdenum separated as completely as possible by levigation, from the heavier red crystalline scales of tetrasulphide of molybdenum, combined with sulphide of potassium. The latter compound is collected on a filter and washed with cold water, till the filtrate no longer gives a blackish brown, but a pure red precipitate with hydrochloric acid. The red scales remaining on the filter are then treated with boiling water, which leaves an insoluble residue of bisulphide of molybdenum; the dark red solution obtained is precipitated by hydrochloric acid in excess; and the precipitated tetrasulphide of molybdenum is thrown on a filter and purified by washing with water. (Berzelius.)

Recently prepared tetrasulphide of molybdenum presents the appearance of a dark red, translucent, bulky precipitate; it shrinks up considerably when dried, and forms a grey, coarsely granular mass, having a metallic lustre, and yielding a cinnamon-brown powder when ground up with water. (Berzelius.)

	Calculation.		Berzelius.
Mo	48	42·86	
4S	64	57·14	56·0 to 55·8
MoS^4	112	100·00	

When distilled alone, it yields a small quantity of sulphurous acid and water (whence, also, Berzelius in his analysis obtained too small a quantity of sulphur), and then sulphur; leaving bisulphide of molybdenum. It is not decomposed either by boiling water or by acids. (Berzelius.)

Tetrasulphide of molybdenum combines with the more basic metallic sulphides, forming *Per-sulphomolybdates* or *Molybdo-persulphites.*

Preparation.—1. By the method given for that of tetrasulphide of molybdenum (*vid. suprà*).—2. When bisulphide of molybdenum in excess is boiled with a concentrated solution of potash and the mixture filtered after cooling, a slightly coloured solution is obtained; and a mixture of bisulphide of molybdenum with per-sulphomolybdate of potash (KS, MoS^4)

remains on the filter; the latter may be separated by solution in boiling water.—3. By double decomposition.

The metallic per-sulphomolybdates are pulverulent, rarely crystalline, and of a red or reddish yellow colour.

They are all decomposed when strongly heated by themselves. Only the compounds of tetrasulphide of molybdenum with the sulphides of ammonium, potassium, sodium, and lithium are soluble in water. In cold water, indeed, they are but very slightly soluble; but in hot water they dissolve and form deep red solutions which do not yield any deposit on cooling. These solutions, when mixed with a stronger acid, give off sulphuretted hydrogen, and yield a precipitate of tetrasulphide of molybdenum. (Berzelius.)

If a double salt of hydrosulphuric acid is supposed to exist in the aqueous solution, that salt must contain an oxide of molybdenum MoO^4 hitherto unknown: *e. g.*, $KS,MoS^4+5HO = KO,HS+MoO^4,4HS$.

D. SULPHATE OF MOLYBDOUS OXIDE.—*a. Basic Sulphate.*—1. Formed by mixing hydrated molybdous oxide in excess with aqueous sulphuric acid.—2. By evaporating a solution of the neutral salt, and decomposing the residue with water.—3. By adding ammonia to the acid solution of *c.* Greyish brown, blistered mass, insoluble in water.

b. Neutral Sulphate.—Formed when the dry hydrated protoxide is rubbed up in a mortar with an equivalent quantity of sulphuric acid. Pitch-black, tenacious mass; decomposed by water into an insoluble basic and a soluble acid salt.

c. Acid Sulphate.—Prepared by decomposing *b* with water, or by dissolving hydrated molybdous oxide in aqueous sulphuric acid. The nearly black solution yields on evaporation a black, tenacious, uncrystallizable mass. This when strongly heated gives off sulphurous acid, and is first converted into sulphate of molybdic oxide, and lastly into a blue compound of sulphuric acid with the blue oxide. The acid salt, mixed with an additional quantity of sulphuric acid, assumes a purple colour after a while. (Berzelius.)

E. SULPHATE OF MOLYBDIC OXIDE.—Formed by dissolving molybdenum in hot oil of vitriol, or in a mixture of dilute sulphuric and nitric acid; or the hydrated molybdic oxide in dilute sulphuric acid; or by heating bichloride of molybdenum with sulphuric acid.—The anhydrous salt is black; but when evaporated to dryness at a very high temperature, it assumes a light blue colour. It dissolves in water, yielding a red solution. (Berzelius.)

F. SULPHATE OF MOLYBDIC ACID.—*a. Basic Sulphate.*—By boiling dilute sulphuric acid with an excess of molybdic acid, a turbid, milky liquid is obtained, which gelatinizes on cooling, and deposits pale yellow flakes of a basic compound, which is sparingly soluble in water but not in alcohol; though the latter colours it green. (Berzelius.)

b. Acid Sulphate.—A solution of molybdic acid (not in excess) in dilute sulphuric acid has a light yellow colour, and dries up to a lemon-yellow, crystalline mass, which deliquesces in the air, but is only partially soluble in water. (Berzelius.)—The solution of molybdic acid in sulphuric acid does not yield crystals on evaporation; but when molybdate of baryta is decomposed by excess of dilute sulphuric acid, and the clear solution evaporated over oil of vitriol, crystals are obtained. (Anderson, *Jahresber.*, 22, 161.)

	Calculation.		Anderson.
MoO^3	72	34·29	32·8
$3SO^3$	120	57·14	57·3
$2HO$	18	8·57	9·9
$MoO^3, 3SO^3 + 2Aq$	210	100·00	100·0

MOLYBDENUM AND IODINE.

A. HYDRATED PROTIODIDE OF MOLYBDENUM, or HYDRIODATE OF MOLYBDOUS OXIDE.—Iodine has no action on ignited molybdenum. By dissolving the hydrated protoxide in aqueous hydriodic acid, a compound is obtained, which behaves in all respects like the protochloride of molybdenum. (Berzelius.)

B. HYDRATED BINIODIDE OF MOLYBDENUM, or BIHYDRIODATE OF MOLYBDIC OXIDE.—Hydrated molybdic oxide forms a red solution with aqueous hydriodic acid. This solution, when spontaneously evaporated in the air, leaves a crystalline residue, which appears red by transmitted and brown by reflected light; is resolved by heat into volatile hydriodic acid and fixed molybdic oxide; and is perfectly soluble in water. (Berzelius.)

MOLYBDENUM AND CHLORINE.

A. PROTOCHLORIDE OF MOLYBDENUM.—Molybdenum heated nearly to redness absorbs the vapour of bichloride of molybdenum passed over it, and is converted into a hard, compact mass, which appears dark red when cold. From this substance, water extracts only a small quantity of protochloride of molybdenum, assuming at the same time a light purple colour; the remaining red protochloride is insoluble in boiling water and hydrochloric acid, but is resolved by solution of caustic potash into chloride of potassium and pure hydrated molybdous oxide. Ignited in a tube, the upper end of which is drawn out to a fine point, it sublimes in the form of a dark brick-red, confusedly crystallized mass, which (with the exception of a small quantity of bichloride of molybdenum produced by the action of the air) resembles the unsublimed chloride in its insolubility in water, and likewise in being decomposed by potash. The red protochloride of molybdenum, on the contrary, when ignited out of contact of air, yields a dark green sublimate, which dissolves in water in the form of hydrochlorate of the protoxide, and has precisely the same composition as the red compound.—Protochloride of molybdenum has therefore two isomeric modifications like the sesqui-chloride of chromium. (Berzelius.)

Hydrated Protochloride of Molybdenum, or *Hydrochlorate of Molybdous Oxide.*—Formed by saturating aqueous hydrochloric acid with the hydrated protoxide. The solution, which has a very dark brown colour, yields on evaporation a black mass, which is tenacious at first, but afterwards becomes brittle; redissolves almost entirely in water; but, on further drying in vacuo, gives off hydrochloric acid and water, and is converted into a black, pulverulent, insoluble compound of protoxide and protochloride of molybdenum. (Berzelius.)

B. BICHLORIDE OF MOLYBDENUM.—Chlorine gas does not act on molybdenum at ordinary temperatures. When molybdenum is gently heated in chlorine gas free from atmospheric air, its surface exhibits a transient glow, and a dark red vapour is formed, which condenses into blackish grey crystals, having a metallic lustre and strongly resembling crystals of iodine. Bichloride of molybdenum is very fusible and again forms crystals on solidifying; sublimes at a gentle heat; fumes in the air and then deliquesces; dissolves in water with so much evolution of heat that the liquid boils. When kept in a vessel containing air, it gradually absorbs oxygen, and yields a white sublimate of molybdate of terchloride of molybdenum. [Should not $MoCl^3$ be set free at the same time? $6MoCl^2 + 6O = MoCl^3, 2MoO^3 + 3MoCl^3$.] It combines with sal-ammoniac, but not with the chlorides of potassium and sodium. (Berzelius.)

Hydrated Bichloride of Molybdenum, or *Bihydrochlorate of Molybdic Oxide.*—1. When bichloride of molybdenum deliquesces in the air, it forms a liquid which is first black, then bluish green, and, as it absorbs more water, becomes greenish yellow, then rust-coloured, and lastly yellow.—2. The hydrated oxide may also be dissolved at once in hydrochloric acid, or metallic molybdenum in hydrochloric acid to which a few drops of nitric acid are added. The concentrated solution remains tolerably permanent in the air, and, on evaporation, leaves black bichloride of molybdenum; but a dilute solution oxidizes when exposed to the air, becoming first green, and then blue. (Berzelius.)

A corresponding solution of the blue oxide of molybdenum in hydrochloric acid is obtained by treating the metal with chlorine-water—by heating the hydrochlorate of molybdic acid with molybdenum, molybdous oxide, molybdic oxide, zinc, tin, or alcohol—or by treating it with a small quantity of hydrosulphuric acid, &c. It has a splendid deep blue colour, which gradually disappears in the air, from oxidation. When boiled with potash, it yields a brown precipitate of the hydrated oxide, while molybdate of potash remains in solution.

C. HYDRATED OXYCHLORIDE OF MOLYBDENUM, or *Mono(?)hydrochlorate of Molybdic Oxide.*—Probably $MoO^2, MoCl^2$ or MoO^2, HCl.—Aqueous hydrochloric acid, or an aqueous solution of bichloride of molybdenum is completely saturated with the hydrated binoxide. The resulting solution leaves, by spontaneous evaporation, a dark, amorphous mass, which readily becomes blue, and is very soluble in water.

D. MOLYBDATE OF TERCHLORIDE OF MOLYBDENUM.—H. Rose discovered the true nature of this compound, which had previously been regarded as terchloride of molybdenum.—1. When dry chlorine gas is passed over heated anhydrous molybdic oxide, the compound is obtained in the form of a sublimate. (Berzelius.)—$3MoO^2 + 3Cl = MoCl^3, 2MoO^3$. The oxide must be prepared by imperfectly reducing warm molybdic acid by hydrogen gas; that obtained by igniting molybdate of soda with sal-ammoniac (IV., 51, 4) appears to be mixed with metallic molybdenum; and accordingly, when treated with chlorine, yields bichloride of molybdenum at the same time. (H. Rose.)—2. A mixture of molybdic acid, sulphuric acid, and sulphate of potash, is evaporated in a retort till no more sulphuric acid is evolved; common salt is then added, and the whole heated to the point of sublimation. But the compound thus obtained is brown, and, towards the end of the process, becomes mixed with bichloride of molybdenum. A solution of molybdic acid in oil of vitriol does not yield any molybdate of chloride of molybdenum by distillation with common salt, but only hydrochloric acid, followed by sulphuric acid containing traces of molybdic acid. (H. Rose.)

Yellowish white, delicate, crystalline scales, which are infusible, but volatilize at a temperature below redness, though with less facility than bichloride of molybdenum. Taste—pungent, rough, bitter, and slightly acid. Easily soluble in water, and likewise soluble in alcohol. (Berzelius.)

	Calculation.		H. Rose.
3Mo	144·0	48·29	48·22
3Cl	106·2	35·61	35·66
6O	48·0	16·10	16·12
$MoCl^3, 2MoO^3$	298·2	100·00	100·00

The compound may also be regarded as $MoClO^2$—that is to say, as molybdic acid in which one atom of oxygen is replaced by one atom of chlorine.

E. **Hydrochlorate of Molybdic Acid.**—Prepared by dissolving the molybdate of bichloride of molybdenum in water, or molybdic acid in hydrochloric acid.

Molybdenum and Fluorine.

A. **Hydrated Protofluoride of Molybdenum,** or **Hydrofluate of Molybdous Oxide.**—The beautiful purple-red solution of hydrated molybdous oxide in aqueous hydrofluoric acid dries up, when moderately heated, to a purple-red varnish, which, at a higher temperature, becomes brown, and is then no longer completely soluble in water. (Berzelius.)

B. **Hydrated Bifluoride of Molybdenum,** or **Bihydrofluate of Molybdic Oxide.**—The solution of hydrated molybdic oxide in aqueous hydrofluoric acid is red, unless the acid is in very large excess, in which case it is almost colourless. After gentle evaporation, whereby it is soon turned blue if the acid is not in excess, it leaves a black, crystalline residue (of bifluoride of molybdenum?), which redissolves perfectly in water, forming a red solution, but loses acid if somewhat more strongly heated, and, when dissolved in water, leaves a residue of molybdic oxide. (Berzelius.)

The blue oxide of molybdenum yields with hydrofluoric acid a deep blue solution which does not crystallize. (Berzelius.)

C. **Hydrated Terfluoride of Molybdenum,** or **Hydrofluate of Molybdic Acid.**—Molybdic acid dissolves readily and abundantly in aqueous hydrofluoric acid. The colourless solution has a sour and disagreeable metallic taste, and yields, on evaporation, a yellowish syrup which exhibits no signs of crystallization; assumes a greenish or bluish tint when heated, in consequence of minute organic particles falling into it; redissolves but imperfectly in water after being evaporated to complete dryness; and leaves an insoluble compound of molybdic acid with a small proportion of hydrofluoric acid, or of molybdic acid with terfluoride of molybdenum, which, though soluble to a certain extent in pure water, is precipitated from it by the first-mentioned acid solution.

Several combinations exist of terfluoride of molybdenum with the more basic metallic fluorides; they are not, however, known in the free state, but only in combination with salts of molybdic acid: *e. g.*, KO,MoO^3+KF,MoF^3. (Berzelius.)

MOLYBDENUM AND NITROGEN.

A. NITRATE OF MOLYBDOUS OXIDE.—Hydrated molybdous oxide forms with dilute nitric acid a dark solution which rapidly becomes purple-red. If an excess of the hydrated oxide is present, a *basic salt* is produced. In both compounds, the oxide is rapidly converted into molybdic acid, the change being marked by decolorization of the salt. (Berzelius.)

B. NITRATE OF MOLYBDIC OXIDE.—Formed by digesting dilute nitric acid with hydrated molybdic oxide, or with excess of molybdenum. The reddish brown solution can only be evaporated to a certain point; when further concentrated, it first turns blue, then becomes colourless, evolves nitric oxide, and leaves a residue of molybdic acid. (Berzelius.)

C. NITRATE OF MOLYBDIC ACID.—Prepared by dissolving metallic molybdenum or molybdic acid, not in excess, in nitric acid. The solution is of a reddish brown colour, has a feebly acid, and subsequently bitter, metallic, astringent taste, and gives off nitric acid when evaporated. (Bucholz.)

Bucholz, by evaporating nitrate of molybdic acid, obtained a dingy reddish yellow residue; by treating it with a small quantity of ammonia, he obtained a brownish red powder mixed with white crystals; and by treating the metal with 3 parts of fuming nitric acid, a pale brownish red mass was produced, with violent effervescence. [Does this consist of molybdic acid united with a small quantity of nitric acid, or contaminated with sesquioxide of iron?]

D. MOLYBDATE OF AMMONIA.—*a. Monomolybdate.*—1. *From the native Sulphide (Wasserblei).* Finely divided sulphide of molybdenum is roasted in a vessel of clay, porcelain, or platinum, with frequent stirring, till the whole of the sulphur is expelled. A strong heat is applied at first, but is afterwards moderated, to prevent the molybdic acid formed from fusing or volatilizing. The molybdic acid which remains is finely pounded and dissolved by long digestion in ammonia. The solution is then filtered and evaporated, by which impurities are separated; filtered again; evaporated to a small bulk; the boiling hot solution mixed with strong ammonia; and the mixture left to crystallize by spontaneous evaporation.—2. *From native Molybdate of Lead (Gelbbleierz).* An intimate mixture of 1 part of the pounded ore with 6 parts of common potash-liver of sulphur is closely pressed into a hessian crucible, the cover of which is then luted down, and the whole exposed for an hour and a half to a strong red heat. The crucible is broken when cold; the reddish brown mass within exhausted with boiling water; the solution filtered; and the sulphide of molybdenum (containing copper and iron) precipitated by dilute sulphuric acid. The sulphide, after being thoroughly washed, is dried and roasted in a porcelain crucible, till it no longer burns with a sulphurous flame; after which, as complete roasting would be too tedious a process, the black residue is dissolved in aqua-regia, filtered, thoroughly washed, and the green filtrate, together with the blue washings, evaporated to dryness. The greenish blue residue is then freed from the hydrochloric and nitric acids by ignition in a porcelain crucible; the remaining yellowish green mass reduced to powder, and digested with aqueous ammonia; the light-blue solution filtered from the brown residue, consisting of sesquioxide of iron with a trace of gypsum; the copper precipitated from the filtrate by a few drops of hydrosulphate of ammonia; and the solution filtered and evaporated to a small bulk. (Wittstein, *Repert.* 73, 155.) Svanberg & Struve prepare the salt by digesting an excess of molybdic acid with strong ammonia in a close vessel, and precipitating with alcohol, and drying the precipitate over quick-lime.

Molybdate of ammonia crystallizes in rectangular prisms united in tufts, and having at first a bitterish saline, and subsequently, an astringent metallic taste. (Brandes.) It contains, according to Brandes, from 75 to 80 per cent. of acid, with from 25 to 20 of ammonia (and water?). When ignited it yields water, nitrogen, and ammonia, leaving a residue of brown oxide of molybdenum, or, if air is admitted, of molybdic acid. It dissolves, according to Brandes, in 2 or 3 parts of water; the solution gives off ammonia when evaporated.

b. Bimolybdate.—Prepared by evaporating the aqueous solution of *a*, without replacing the ammonia which volatilizes. This salt forms a translucent, striated, saline mass; or—when spontaneously evaporated—large crystals, belonging to the oblique prismatic system, having the base obliquely inclined to the obtuse lateral edges, with numerous faces, especially *u, a, f, t*; cleavage distinct parallel to *t*; transparent, with double refracting power; having a pearly lustre in the direction of the *t*-faces; otherwise, with a vitreous lustre; colour bluish-green, but white when reduced to powder. The salt has a saline and metallic taste. (Haidinger, *Edinb. J. of Sc.* 1, 100.) When heated it evolves ammonia, water, and nitrogen gas, and if air be excluded, leaves brown oxide of molybdenum (Berzelius), which, on admission of air, is converted into molybdic acid. According to Bucholz, it leaves an ash-grey coloured, and according to Wittstein, a greyish-blue oxide. It dissolves sparingly and without colour in water. ¶ According to Svanberg & Struve, it is precipitated in the form of a white powder, by rapidly evaporating a solution of molybdic acid in ammonia, of which the liquid should smell permanently. From an ordinary solution of this kind, a compound of bimolybdate and termolybdate of ammonia with 3 atoms of water crystallizes [on cooling?], in colourless and transparent six-sided prisms. Different salts are also obtained by the action of nitric acid on solutions of molybdic acid in ammonia; but they have not been further examined. ¶

c. Hyper acid molybdate?—According to Brandes, this compound is precipitated from a solution of *a* or *b*, on the addition of sulphuric acid, in the form of a white powder, from which the sulphuric acid with the aid of heat, removes every trace of ammonia. Acetic acid in excess, likewise precipitates dazzling white crystals, which disengage ammonia on the addition of potash, and when ignited, first become greyish blue, and then leave 93·9 per cent. of pure molybdic acid. (Wittstein.)

If to a strong solution of molybdate of ammonia a very small quantity of concentrated aqueous phosphoric acid is first added, and then a considerable quantity of hydrochloric, sulphuric, or nitric acid—or one of these acids first, and phosphoric acid afterwards—a lemon-yellow, crystalline powder is precipitated, and with greater rapidity in proportion as the solution is more concentrated. This precipitate, besides molybdic acid, contains a small portion of ammonia, but no phosphoric acid, or at most a mere trace. With potash it evolves ammonia, and forms a colourless liquid, from which, even after long boiling, it is again precipitated by hydrofluoric acid; but if the solution in potash is evaporated to dryness, and the residue dissolved in water, hydrofluoric acid merely produces a yellow colour; but hydrofluoric acid and sal-ammoniac together throw down a yellow powder. The yellow powder yields with hot oil of vitriol, a colourless solution which is not precipitated by water. It does not dissolve perceptibly in cold water, or in dilute sulphuric, hydrochloric, or nitric acid; and but very sparingly in boiling water, to which it does not impart any colour. (Gmelin.) ¶ According to Svanberg & Struve, the yellow powder consists of $NH^4O, 5MO^3+HO$, besides a small quantity of phosphoric acid. By boiling with potash, a colourless solution is obtained, which yields with acids a yellow crystalline precipitate, in which the NH^4O is replaced by KO. A solution of the yellow ammoniacal salt in ammonia gives a white precipitate with chloride of barium, which turns yellow on the addition of an acid. ¶

E. Carbonate of Molybdous Oxide and Ammonia.—Hydrated molybdous oxide does not dissolve in pure ammonia or its carbonate; but when molybdous salts are supersaturated with carbonate of ammonia, the precipitate first formed redissolves, producing a dark brown solution, which, on boiling, again deposits the molybdous oxide as a basic salt. (Berzelius.)

F. Carbonate of Molybdic Oxide and Ammonia. — Hydrated molybdic oxide is soluble in aqueous solution of carbonate of ammonia, and separates again completely when the liquid is boiled. (Berzelius.)

G. Phosphate of Molybdous Oxide and Ammonia.—Molybdous phosphate dissolves in ammonia, forming a blackish brown solution. (Berzelius.)

H. Sulphomolybdate of Ammonium.—NH^4S, MoS^3.—1. Prepared by saturating monomolybdate of ammonia with hydrosulphuric acid and evaporating to a small bulk.—2, By dissolving molybdic acid in bihydrosulphate of ammonia, and expelling the liberated ammonia by evaporation. 3. By dissolving recently precipitated tersulphide of molybdenum in hydrosulphate of ammonia. The solution obtained by either of these methods is mixed in a moderately concentrated state with alcohol. The compound separates in the form of a cinnabar-coloured powder,—or, if the mixture is made with warm solutions, crystallizes on cooling in cinnabar-coloured scales. It becomes dark brown on exposure to the air. Dissolves with facility in water, but very sparingly in alcohol. Its aqueous solution, when spontaneously evaporated, evolves hydrosulphate of ammonia, and deposits round the sides of the vessel a few crystals which reflect light of a green colour; but the greater part dries up to a blackish-grey, brilliant, uncrystallizable compound of hydrosulphate of ammonia with excess of tersulphide of molybdenum, which dissolves rather freely in water, but is very sparingly soluble in alcohol. (Berzelius.)

I. Per-sulphomolybdate of Ammonium.—NH^4S, MoS^4.—Tetrasulphide of molybdenum digested while still moist with hydrosulphate of ammonia containing excess of ammonia, is converted into a yellow powder. The presence of free ammonia renders the new compound less soluble in the liquid. The powder when dried in the air becomes dark red, probably from disengagement of hydrosulphate of ammonia. It dissolves slightly in cold water, forming a yellow solution, and more abundantly in hot water, but is totally insoluble in solution of ammonia. (Berzelius.)

K. Hydrochlorate of Molybdous Oxide and Ammonia.—Dark-coloured, crystallizable double salt. (Berzelius.)

L. Hydrochlorate of Molybdic Oxide and Ammonia.—*a.* An aqueous mixture of bichloride of molybdenum and sal-ammoniac yields by spontaneous evaporation, small, brown crystals which are permanent in the air.—*b.* If bichloride of molybdenum is treated with ammonia till the precipitate first formed just redissolves, and the solution then left to evaporate spontaneously, a black crystalline mass remains which dissolves in water, forming a red solution. (Berzelius.)

M. Monofluoride of Molybdenum and Ammonium, and Hydrofluate of Molybdous Oxide and Ammonia.—*Ammonio-fluoride of Molybdenum.*—Precisely analogous to the potassium compound. (Berzelius.)

N. Bifluoride of Molybdenum and Ammonium, and Hydrofluate of Molybdic Oxide and Ammonia.—*Ammonio-perfluoride of Molybdenum.*—Reddish-yellow mass, more soluble in water than the corresponding potassium compound. (Berzelius.)

Molybdenum and Potassium.

Neither molybdous nor molybdic oxide dissolves in solution of potash. (Berzelius.)

A. Molybdate of Potash.—*a. Monomolybdate.*—Obtained similarly to the molybdate of ammonia,—or, in an impure state, by detonating a mixture of one part of native sulphide of molybdenum (*Wasserblei*) with 3 parts of nitre. Crystallizes in permanent, brilliant needles, which have a rough metallic taste, are fusible, and dissolve readily in water. (Bucholz.) ¶ According to Svanberg & Struve, (*J. pr. Chem.* 44, 257), this salt is best prepared by adding moist termolybdate of potash to a solution of caustic potash in alcohol of 95 per cent. The salt separates in the form of an oily mass at the bottom of the vessel; this, after being washed with alcohol, is left to crystallize under a bell-jar, beside caustic lime and oil of vitriol. Crystallizes in four-sided prisms, with two truncation-surfaces resting on the narrower lateral faces. Readily soluble in water. When heated it loses water, and is converted into a white powder, which fuses at a high temperature, and on cooling solidifies to a crystalline mass. Its formula is $KO,MO^3+\frac{1}{2}HO$.

	Anhydrous.		Svanberg & Struve.
KO	47·20	40·20	40·71
MoO^3	70·06	59·80	59·29
	117·26	100·00	100·00

In this calculation the atomic weight of MO is taken as 46·06. ¶

b. Bimolybdate.—This salt is obtained as a white precipitate, by decomposing a concentrated solution of the salt *a* with sulphuric, hydrochloric, or nitric acid, or chlorine gas. It crystallizes in brilliant, oblique, four-sided laminæ; fuses more readily than molybdic acid, attacking the earthen crucible rapidly, and assuming a fine-yellow colour when cold. It dissolves sparingly in cold water, but in 3 or 4 parts of boiling water. The solution is precipitated reddish-brown by ferrocyanide of potassium. (Bucholz.) Acids throw down the salt from a cold solution. The solution in hot water deposits, on cooling, white bulky flakes of a still more acid salt which does not redissolve in boiling water. (Berzelius.)

¶ Svanberg & Struve did not succeed in obtaining this salt. When strong nitric or hydrochloric acid is cautiously added to a solution of molybdic acid in carbonate of potash, till the resulting precipitate no longer entirely disappears, a compound salt crystallizes out, consisting either of $3(KO, 2MoO^3) + KO, 3MoO^3 + 6HO$, or $3(KO, MoO^3) + 5(KO, 3MoO^3) + 12HO$. It is resolved by water into termolybdate and monomolybdate of potash, which dissolves.

c. Termolybdate of Potash.—$KO, 3MoO^3 + 3HO$.—The most readily prepared of all the compounds which molybdic acid forms with potash. If a solution of molybdic acid in carbonate of potash be treated with hydrochloric acid till it becomes turbid, and then set aside, a mixture of monomolybdate and termolybdate of potash separates after a while in six-sided prisms. (*vid. sup.*) On treating these crystals with water, they are resolved into difficultly soluble termolybdate and easily soluble monomolybdate of potash. The termolybdate forms a bulky white precipitate, which contracts considerably on drying, and consists of microscopic needles. It is soluble in boiling water, from which it separates but slowly. It may also be obtained by adding nitric acid in excess to a saturated solution of molybdic acid in carbonate of potash, washing the precipitate with cold water, then dissolving in boiling water, and crystallizing. The boiling water often leaves a residue consisting sometimes of tetramolybdate, sometimes of pentamolybdate of potash. (Svanberg & Struve.)

d. Tetramolybdate and Pentamolybdate of Potash.—1. The yellow powder obtained by precipitating molybdate of ammonia with phosphoric acid, &c. (p. 67) is heated with solution of potash till the ammonia is expelled. The resulting colourless solution is then mixed with nitric acid, whereby a yellow crystalline precipitate is obtained, the formula of which is $KO, 5MoO^3 + 2HO$.—2. By adding an excess of nitric acid to a solution of molybdic acid in carbonate of potash, sometimes tetramolybdate, sometimes pentamolybdate of potash is precipitated. (*vid. sup.*) Both salts are white, anhydrous, insoluble in water, easily fusible, and solidify in a crystalline mass. (Svanberg & Struve.) ¶

B. CARBONATE OF MOLYBDIC OXIDE AND POTASH.—The recently precipitated hydrate of molybdic oxide dissolves but sparingly in an aqueous solution of carbonate of potash, imparting to it a yellow colour; the anhydrous oxide is totally insoluble. By supersaturating a molybdic salt with carbonate of potash, perfect solution is effected, because an excess of carbonic acid is then present in the liquid. On boiling the solution, a large quantity of the hydrated oxide is thrown down, and carbonic acid is evolved; a portion, however, still remains dissolved. When exposed to the air, the solution becomes colourless in a few days, from formation of molybdate of potash. (Berzelius.)

C. SULPHOMOLYBDATE OF POTASSIUM.—*α. Normal Salt.*—KS, MoS^3.—1. A finely divided mixture of equal weights of carbonate of potash and sulphur, with a small proportion of charcoal and a large excess of native sulphide of molybdenum, is put into a hessian crucible and covered with powdered charcoal. The whole is then exposed to a heat below redness till pentasulphide of potassium is formed—after which it is strongly ignited for three hours, or as long as sulphurous acid continues to be evolved. In this process, one atom of sulphur passes from the pentasulphide of potassium to the bisulphide of molybdenum, and the resulting tersulphide of molybdenum unites with protosulphide of potassium formed by the expulsion of 3 atoms of sulphur. The black, porous, unfused mass is dissolved in water, whereby it becomes heated; the dark red solution, separated by filtration from the unaltered portions of ore, is evaporated in a cylindrical glass vessel at a temperature of 40°; and the crystals obtained are dried between folds of bibulous paper.—2. Monomolybdate of potash is saturated with hydrosulphuric acid and evaporated to the crystallizing point.—A small quantity of this sulphur-salt is also formed by digesting the native sulphide of molybdenum and potassium with an aqueous solution of pentasulphide of potassium. (Berzelius.)

The salt crystallizes in four and eight-sided prisms, sometimes with dihedral summits, in which case it resembles the octohedron; or sometimes (if crystallized from a hot solution) perpendicularly truncated. By reflected light it exhibits a beautiful green, metallic colour, like the wing-cases of many kinds of beetles; by transmitted light it is ruby-red. Fracture uneven and conchoidal, exhibiting a green colour. Its powder is dark-red, but becomes green and lustrous by pressure.

		Crystallized.		Or:			
K	39·2	....	25·92	KS	55·2	....	36·51
Mo	48·0	....	31·75	MoS^3	96·0	....	63·49
4S	64·0	....	42·33				
KS,MoS^3	151·2	....	100·00		151·2	....	100·00

The crystals, when heated in hydrogen gas (or, in short, out of contact of air) become grey; and though about a third of the compound remains undecomposed even at a white heat, the rest appears to be converted into a mixture of bisulphide of molybdenum and bisulphide of potassium, the latter of which, together with the original unaltered sulphur-salt, may be removed by water: $KS,MoS^3 = KS^2 + MoS^2$. The crystals, when decomposed by hydrochloric acid, yield from 49·2 to 49·5 per cent. of chloride of potassium. They dissolve in water, forming a beautiful yellowish red solution, from which alcohol precipitates nearly the whole of the salt, at first in the form of a cinnabar-red powder, afterwards on standing, in cinnabar-red scales, which, when dried, assume a metallic-green colour.—The supernatant alcoholic solution, which is of a fine red colour, yields similar crystals on evaporation. (Berzelius.)

b. With 2 *atoms of sulphur-acid.*—From an aqueous solution of the salt *a*, a portion only of the potassium compound is separated by an acid (the best acid for this purpose is acetic acid added till the liquid reddens litmus, because it does not, like the stronger acids, decompose the compound *b* when added in excess), and the liquid, which is still clear, though of a darker colour, is left to evaporate spontaneously. The solution first assumes a gelatinous consistence, and then leaves a blackish-grey shining mass; or if acetic acid is previously used, the acetate of potash which is formed precipitates the new compound from the concentrated solution as a brownish yellow powder, which on drying becomes greyish black with metallic lustre; dissolves slowly in cold water, with a pale yellow colour, but rapidly in boiling water, producing a dark yellow solution. (Berzelius.)

D. Per-sulphomolybdate of Potassium.—KS, MoS^4.—1. Prepared by the method described (p. 61), the crystals formed being purified from bisulphide of molybdenum either by elutriation, or by solution in water, filtration, and evaporation.—2. A dilute aqueous solution of the compound of protosulphide of potassium with excess of tersulphide of molybdenum (C. *b*) is heated to a temperature of 60° or 80°; whereupon the liquid, under the influence of the air, becomes turbid and deposits the persulphomolybdate of potassium.—3. Tetrasulphide of molybdenum is digested, while still moist, with an aqueous solution of bihydrosulphate of potash. The portion which first dissolves is again deposited, and after a short time the liquid loses its colour, and the mass is converted into a reddish-yellow powder.—When tersulphide of molybdenum is mixed with the tetrasulphide, the former remains dissolved, imparting a reddish-yellow colour to the liquid; by this means, the two sulphides of molybdenum may be easily separated. (Berzelius.)

When prepared by the first method, the compound has the form of small, rectangular, ruby-red, transparent scales, transversely striated on the longer faces. The second method yields it in the form of a pulverulent precipitate, which unites on the filter into a reddish-yellow mass, consisting of small, silky, crystalline particles. When obtained by evaporating the aqueous solution, it forms a transparent red mass of the consistence of an extract. The crystals, when gently ignited, decrepitate slightly, giving off water and minute quantities of sulphur and hydrosulphuric acid,—and are resolved into a grey shining mixture of bisulphide of molybdenum in crystalline scales and tersulphide of potassium, the latter of which may be removed by water. $KS,MoS^4 = KS^3 + MoS^2$. This compound dissolves but very sparingly in cold water, forming a pale yellow solution, and is insoluble in a cold solution of potash; boiling water dissolves it with a red colour, and does not deposit it again on cooling. Hydrochloric acid added to the solution precipitates tetrasulphide of molybdenum. (Berzelius.)

E. Sulphate of Molybdic Oxide and Potash.—Molybdic oxide dissolves slowly in bisulphate of potash, when fused with it in a close vessel. The compound is readily soluble in water, forming a yellow solution. (Berzelius.)

F. Protochloride of Molybdenum and Potassium, and Hydrochlorate of Molybdous Oxide and Potash.—Formed when the black liquid obtained by the action of amalgam of potassium on a solution of protochloride of molybdenum (p. 49) is evaporated to the crystallizing point.—Black, efflorescent salt, which, when redissolved in water, leaves a black powder, probably a basic salt. (Berzelius.)

G. Protofluoride of Molybdenum and Potassium, and Hydrofluate of Molybdous Oxide and Potash.—*Molybdo-fluoride of Potassium.*—Precipitated in pale rose-coloured flakes on mixing the aqueous solutions of protofluoride of molybdenum and hydrofluate of potash. These flakes dissolve in water containing hydrochloric acid, and separate again on evaporation or simple cooling, in the form of a dark rose-coloured powder, which becomes paler when dried. (Berzelius.)

H. Bifluoride of Molybdenum and Potassium, and Hydrofluate of Molybdic Oxide and Potash.—*Permolybdo-fluoride of Potassium.*—

An aqueous solution of hydrofluate of potash precipitates from a solution of hydrofluate of molybdic oxide a reddish-brown powder, sparingly soluble in water. (Berzelius.)

I. SULPHOMOLYBDATE OF POTASSIUM WITH NITRE.—When equal weights of the two salts are dissolved in water and the solution left to evaporate spontaneously, green crystals are obtained, possessing the metallic lustre, and closely resembling those of sulpho-molybdate of potassium: they explode like gunpowder when heated. (Berzelius.)

MOLYBDENUM AND SODIUM.

A. MOLYBDATE OF SODA.—*a. Monomolybdate.*—Prepared in a similar manner to molybdate of potash.—Forms large efflorescent crystals, having a rough taste, fusing readily, but not volatile.—According to Brandes, 70·37 parts of acid are required to neutralize 29·63 parts of soda.—The salt is not decomposed at a red heat. Acids precipitate from it an acid salt. It is very soluble in water.

¶ By fusing 5·491 parts of molybdic acid with 4·074 parts of carbonate of soda, a mixture is obtained which solidifies in a crystalline mass on cooling; it is very soluble in water; crystallizes from an aqueous solution by evaporation in small rhombohedrons; and contains 30·36 per cent. of soda: $NaO, MoO^3 + 2HO$.

b. Bimolybdate of Soda.—$NaO, 2MoO^3 + HO$.—Prepared by fusing 2·4325 parts of molybdic acid with 0·919 parts of carbonate of soda. Difficultly soluble in cold water after ignition. Dissolves in hot water after a considerable time. Contains 18·20 per cent. of soda.

c. Termolybdate of Soda.—$NaO, 3MoO^3 + 7HO$.—Nitric acid is added to a saturated solution of molybdic acid in carbonate of soda till the liquid acquires an acid reaction. After some time, a voluminous precipitate of the termolybdate is deposited. More soluble in water than the bimolybdate. Contains 13·24 per cent. of soda. Molybdic acid is not precipitated from solutions of its soda-salts by excess of nitric acid, except with the aid of heat. (Svanberg & Struve.) ¶

Molybdic acid heated with carbonate of soda on platinum before the blowpipe, effervesces, and forms a bead which is clear while hot, but becomes milk-white on cooling. In the inner flame the bead becomes brown, and is transparent while hot, but turbid or opaque when cold; and if it contains a rather large proportion of molybdic acid, likewise becomes charged in the inner flame with brown oxide and reduced metal. On charcoal, the first portions are absorbed, and reduced to the metallic state within the substance of the charcoal: if fresh molybdic acid is then laid on the charcoal, together with a small quantity of carbonate of soda, and exposed to a powerful reducing flame, a bead is obtained, consisting of metallic molybdenum and molybdate of soda, separable by means of water. (Berzelius.)

B. CARBONATE OF MOLYBDIC OXIDE AND SODA.—Prepared like the corresponding potash compound. (Berzelius.)

C. Borax on platinum in the outer blowpipe-flame forms with molybdic acid a transparent and colourless glass. This glass, when exposed to the inner flame on charcoal, becomes dirty brown; and if it contains a rather large quantity of molybdic acid, becomes turbid, and deposits numerous brown flakes of molybdic oxide. (Berzelius.)

D. Microcosmic salt forms with molybdic acid on platinum in the outer blowpipe-flame a transparent glass, which is green while hot, and colourless when cold. It may also be obtained colourless while hot by prolonged exposure in the outer flame. In the inner flame or on charcoal it appears black or dark blue and opaque while hot, and on cooling assumes a splendid green colour and becomes transparent. (Berzelius.)

E. SULPHOMOLYBDATE OF SODIUM.—NaS, MS^3.—An aqueous solution of monomolybdate of soda is saturated with hydrosulphuric acid, and evaporated to a small bulk. The whole becomes converted into a mass of small, granular, dark red crystals. Sometimes also slender needles are obtained as the liquid cools; these, after being dried on bibulous paper, appear green by reflected light. The compound is decomposed by ignition, like the potassium salt, but much more completely. By repeated solution in water and recrystallization, it acquires a light red colour and radiated structure, in consequence of the production of molybdate of soda. It is not precipitated from an aqueous solution by alcohol, or at most to a very slight extent. (Berzelius.)

b. With two atoms ? of Sulphur-acid.—Prepared in a similar manner to the potassium compound, which it exactly resembles. Dissolves slowly in water. (Berzelius.)

F. PER-SULPHOMOLYBDATE OF SODIUM.—Prepared similarly to the corresponding potassium compound, with which it agrees in physical and chemical properties; it cannot however be crystallized, but forms a reddish yellow powder sparingly soluble in cold water, but readily dissolving by boiling water. (Berzelius.)

G. FLUORIDE OF MOLYBDENUM AND SODIUM, and HYDROFLUATE OF MOLYBDOUS OXIDE AND SODA.—More soluble than the potassium salt; it is deposited on evaporation as a rose-coloured, crystalline powder. (Berzelius.)

H. BIFLUORIDE OF MOLYBDENUM AND SODIUM, and HYDROFLUATE OF MOLYBDIC OXIDE AND SODA.—Behaves in a similar manner to the corresponding ammoniacal salt. (Berzelius.)

MOLYBDENUM AND LITHIUM.

A. SULPHOMOLYBDATE OF LITHIUM.—The aqueous solution yields on evaporation a brown syrupy liquid, which slowly dries up to a dark red, amorphous mass. When heated, this substance is completely resolved. into bisulphide of molybdenum and bisulphide of lithium; the latter of which may be removed by water. The compound does not deliquesce in the air, but dissolves very easily in water. It likewise enters into combination with excess of tersulphide of molybdenum. (Berzelius.)

B. PER-SULPHOMOLYBDATE OF LITHIUM.—Pale yellow, somewhat crystalline powder, which is slightly soluble in cold water, and dissolves readily in boiling water, forming a red solution. The latter solution deposits nothing on cooling, but when evaporated leaves a red residue of the consistence of extract. (Berzelius.)

MOLYBDENUM AND BARIUM.

A. MOLYBDATE OF BARYTA.—*a. Dimolybdate.*—Precipitated from a solution of *b* in dilute nitric acid, by supersaturating the liquid with ammonia. Forms a white powder, which also remains white after ignition; soluble in dilute hydrochloric or nitric acid.

For the preparation of this salt, the pigs of iron obtained from the Mansfeld copper furnaces may be used. For this purpose they are reduced to powder; fused with carbonate of soda; the fused mass exhausted with water; the filtrate supersaturated with nitric acid, warmed to expel carbonic acid, and mixed with nitrate of baryta; the liquid then filtered from sulphate of baryta; and the dimolybdate of baryta precipitated by ammonia and washed with cold water. (Heine, *J. pr. Chem.* 9, 204.) [Is not *vanadic acid* concerned in this action?] (Svanberg & Struve doubt the existence of this salt.)

	After ignition.		Heine.
2BaO	153·2	68·03	68·04
MoO^3	72·0	31·97	31·96
$2BaO, MoO^3$	225·2	100·00	100·00

	Dried at 80°.		Heine.
2BaO	153·2	65·41	64·72
MoO^3	72·0	30·75	30·39
HO	9·0	3·84	4·89
+ Aq	234·2	100·00	100·00

b. Monomolybdate.—Molybdate of potash throws down from a solution of acetate of baryta a white flocculent precipitate, which rapidly condenses to a crystalline powder. This compound turns blue on ignition. (Berzelius.) It dissolves in hydrochloric or nitric acid, which then by spontaneous evaporation deposits the salt in the form of a crystalline crust. It is insoluble in water. According to Brandes, it contains 51·55 per cent. of baryta to 48·45 of molybdic acid.

¶ According to Svanberg & Struve, molybdic acid forms a great number of salts with baryta.

The normal salt is prepared by precipitating a solution of molybdic acid in excess of ammonia by chloride of barium. Fine, crystalline powder, sparingly soluble in water; infusible. Contains 52·17 per cent. of baryta. If the yellow ammoniacal compound (p. 67) be dissolved in ammonia, and chloride of barium added, a white precipitate is obtained, which behaves like the monomolybdate, excepting that it assumes a yellow colour when treated with acids. It contains 50·07 per cent. of baryta, 1·83 of ammonia, 46·77 of molybdic acid, and 1·09 of phosphoric acid; hence it appears to be monomolybdate of baryta with small quantities of ammonia and phosphoric acid.

c. Five-halves Molybdate of Baryta. — $2BaO, 5MoO^3 + 6HO$, or $(BaO, 2MoO^3) + (BaO, 3MoO^3) + 6HO$.—Obtained from the corresponding ammoniacal salt in the form of a white flocculent precipitate. Uncrystallizable; rather soluble in water; fusible; the fused salt solidifies in a crystalline form.

d. Termolybdate of Baryta.—$BaO,3MoO^3 + HO$.—A corresponding alkaline salt is precipitated by chloride of barium. White, flocculent precipitate, soluble to a certain extent in water. When dry, it forms a yellowish, white, horny mass. Fuses at a red heat, and solidifies on cooling to a crystalline mass. Contains 26·66 per cent of baryta.

e. Nonomolybdate of Baryta.—$BaO, 9MoO^3 + 4HO$.—Prepared from the normal salt by treating it with dilute nitric acid. Crystallizes in small, six-sided prisms; insoluble in water; infusible. ¶

B. Sulphomolybdate of Barium.—Sulphide of barium is boiled with water and excess of tersulphide of molybdenum—the solution filtered boiling hot into a hot glass vessel—and left to cool. After a short time, numerous brownish red, brilliant crystals appear, which, when laid on paper, crumble to a shining, reddish-yellow powder. When gently heated they give off water and become red; they are not decomposed by cold concentrated hydrochloric acid, but somewhat readily by dilute hydrochloric acid, sulphuretted hydrogen being evolved and tersulphide of molybdenum precipitated. The crystals consist of $BaS,3MoS^3$.—The mother-liquid poured off from the salt and again evaporated, yields a further quantity of crystals, and then dries up to a dark red, translucent, uncrystallizable mass, composed of BaS,MoS^3. (Berzelius.)

C. Per-sulphomolybdate of Barium.—The corresponding potassium compound produces with chloride of barium a yellowish-red precipitate, which is not decomposed by dilute hydrochloric acid, and is insoluble in water, which, however, makes it denser and gives it a cinnabar colour. (Berzelius.)

Molybdenum and Strontium.

A. Molybdate of Strontia.—Insoluble in water.

B. Sulphomolybdate of Strontium.—The compounds, SrS,MoS^3 and $SrS, 3MoS^3$, possess similar properties to the corresponding compounds of barium. (Berzelius.)

C. Per-sulphomolybdate of Strontium.—Prepared like the barium compound. (Berzelius.)

Molybdenum and Calcium.

A. Molybdate of Lime.—Molybdate of potash precipitates from a solution of chloride of calcium a white powder, insoluble in water but soluble in hydrochloric acid.

B. Sulphomolybdate of Calcium.—By proceeding as in the preparation of the barium compound above described, small, delicate, brilliant, transparent, cinnabar-coloured needles, *a*, are obtained, which are permanent in the air even at 100°, and are blackened by hydrochloric acid from separation of tersulphide of molybdenum; they consist of $CaS,3MoS^3$.—*b*. The mother-liquid leaves on evaporation, a dark red, translucent varnish $= CaS,MoS^3$. (Berzelius.)

C. PER-SULPHOMOLYBDATE OF CALCIUM.—When the corresponding potassium salt is mixed in solution with chloride of calcium and alcohol added, the liquid becomes slightly turbid, and in the course of twelve hours deposits a scarlet powder sparingly soluble in water. (Berzelius.)

MOLYBDENUM AND MAGNESIUM.

A. MOLYBDATE OF MAGNESIA.—Prepared by boiling magnesia with molybdic acid and water. Crystallizes in small, white, four-sided prisms united together in cauliflower-like masses, which are permanent in the air, and have at first a bitterish, afterwards an astringent metallic taste. The crystals when ignited, give off their water of crystallization (amounting, according to Berzelius, to 28 per cent., or 4 atoms), and are converted into a yellow mass; they dissolve in 12 or 15 parts of cold water. (Brandes.) The anhydrous salt contains 22·15 per cent. of earth to 77·83 of acid; the crystallized salt 15·5 of earth, 54·5 of acid, and 30·0 of water. (Brandes.)

B. SULPHOMOLYBDATE OF MAGNESIUM.—Formed by boiling tersulphide of molybdenum with an aqueous solution of bihydrosulphate of magnesia. The filtrate as it cools deposits a dark-brown, pulverulent compound of sulphide of magnesium with more than one atom of tersulphide of molybdenum, while the mother-liquid dries up to a dark-red varnish, which contains the two metallic sulphides in atomic proportions. (Berzelius.)

C. PER-SULPHOMOLYBDATE OF MAGNESIUM.—Prepared by double decomposition. Forms a red precipitate, insoluble in water. (Berzelius.)

MOLYBDENUM AND CERIUM.

A. MOLYBDATE OF CEROUS OXIDE.—Precipitated from a solution of a cerous salt by an alkaline molybdate, in white flakes which are insoluble in water but dissolve in several of the acids. (Hisinger & Berzelius.)

B. CEROUS SULPHOMOLYBDATE.—CeS, MoS^3.—The corresponding potassium compound dissolved in water, produces with a salt of cerous oxide, a blackish-grey precipitate, which, after drying, forms a dark brown powder. (Berzelius.)

C. CERIC SULPHOMOLYBDATE.—$Ce^2S^3,3MoS^3$.—Prepared by precipitating a salt of the sesquioxide of cerium as above. Only a portion of the compound is thrown down as a brown precipitate; the greater part remains dissolved, and produces a dark reddish-yellow solution. From this solution, ammonia throws down a more basic compound in the form of a brown viscid mass, which stops up the pores of the filter. (Berzelius.)

D. CEROUS PER-SULPHOMOLYBDATE, and CERIC PER-SULPHOMOLYBDATE.—Prepared by precipitating cerous and ceric salts by a solution of tetrasulphide of molybdenum. Red precipitate. (Berzelius.)

MOLYBDENUM AND YTTRIUM.

A. MOLYBDATE OF YTTRIA.—Molybdate of ammonia gives with salts of yttria a white curdy precipitate which dries up to a white powder. The salt is insoluble in water, but dissolves readily in nitric acid. (Berlin.)

B. SULPHOMOLYBDATE OF YTTRIUM.—An aqueous solution of sulphomolybdate of potassium does not precipitate acetate of yttria. The liquid becomes colourless in the course of twelve hours, and deposits tersulphide of molybdenum. (Berzelius.)

C. PER-SULPHOMOLYBDATE OF YTTRIUM.—Formed by precipitating a salt of yttria by an aqueous solution of the potassium compound. Red powder. (Berzelius.)

MOLYBDENUM AND GLUCINUM.

A. SULPHOMOLYBDATE OF GLUCINUM.—Prepared like the yttrium compound. The mixture, however, deposits the tersulphide of molybdenum more slowly, and consequently retains its red colour for a longer time. (Berzelius.)

B. PER-SULPHOMOLYBDATE OF GLUCINUM.—Prepared by the same method as the yttrium compound.

MOLYBDENUM AND ALUMINUM.

The aqueous solution of sulphomolybdate of potassium mixed with salts of alumina gives off hydrosulphuric acid, and forms an immediate precipitate, consisting of a mixture of tersulphide of molybdenum and hydrate of alumina. When a solution of per-sulphomolybdate of potassium is mixed with a salt of alumina, a red liquid is produced which appears to be clear, but when filtered leaves the colouring matter on the filter. (Berzelius.)

MOLYBDENUM AND THORINUM.

MOLYBDATE OF THORINA.—Alkaline monomolybdates and bimolybdates produce in salts of thorina a white flocculent precipitate, (Berzelius.)

MOLYBDENUM AND SILICIUM.

A. SILICATE OF MOLYBDOUS OXIDE.—Precipitated on mixing the double fluoride of silicium and molybdenum with ammonia in dark brown flakes, from which the ammoniacal solution gradually removes the protoxide, leaving pure silica below. (Berzelius.)

B. SILICATE OF MOLYBDIC OXIDE.—Prepared by decomposing the hydrofluate of silica and molybdic oxide with ammonia. Its behaviour is similar to that of the preceding compound. (Berzelius.)

C. HYDROFLUATE OF SILICA AND MOLYBDOUS OXIDE.—*Molybdofluoride of Silicium.*—A solution of the hydrated protoxide in excess of hydrofluosilicic acid, does not dry up in the air at ordinary temperatures; but when gently heated it parts with its excess of acid, and yields a black neutral compound, which redissolves in the aqueous acid. (Berzelius.)

D. HYDROFLUATE OF SILICA AND MOLYBDIC OXIDE. — *Bimolybdofluoride of Silicium.*—The acid aqueous solution, when spontaneously evaporated, acquires a bluish tinge, and yields a black uncrystallizable mass, from which water dissolves out the blue salt, leaving the neutral compound in the form of a jet-black powder. This powder is resolved by the prolonged action of the water into an acid salt which dissolves, and an insoluble basic compound. By ammonia, which withdraws the hydrofluoric acid, it is converted into silicate of molybdic oxide. In acidulated water it dissolves without decomposition. (Berzelius.)

E. HYDROFLUATE OF MOLYBDIC ACID AND SILICA.—*Permolybdo-fluoride of Silicium.*—With molybdic acid, hydrofluosilicic acid forms a yellowish solution. This solution when evaporated, leaves a lemon-yellow, opaque substance, which redissolves for the most part in water, forming a yellow solution, a small quantity of a *basic* compound being left behind. (Berzelius.)

MOLYBDENUM AND TITANIUM.

Sulphomolybdate of potassium in solution, behaves with salts of titanium in the same manner as with salts of aluminum. (Berzelius.)

MOLYBDENUM AND TUNGSTEN.

A. TUNGSTATE OF MOLYBDIC OXIDE.—Tungstate of ammonia forms with bichloride of molybdenum, a deep purple-red solution, from which, when concentrated, sal-ammoniac throws down a red compound, so that the liquid itself retains only a pale yellow colour. The precipitate collected on a filter and washed, first with water containing sal-ammoniac, and then with alcohol of specific gravity 0·87, and lastly pressed and dried at a gentle heat, exhibits a dark purple colour, is permanent in the air, and perfectly soluble in water. A dilute solution gradually becomes colourless in the air, from formation of molybdate of tungstic acid; soda precipitates molybdic oxide from it. (Berzelius.)

B. BASIC TUNGSTATE OF MOLYBDIC OXIDE AND AMMONIA.—An aqueous solution of A is instantaneously decolorized by ammonia, and deposits, after a while, a white powder insoluble in water, from which soda separates molybdic oxide. (Berzelius.)

MOLYBDENUM AND MOLYBDENUM.

FLUORIDE OF MOLYBDENUM AND POTASSIUM, WITH MOLYBDATE OF POTASH.—In the crystallized state, composed of KO,MoO^3+KF,MoF^3+2Aq. —1. Prepared by mixing an aqueous solution of hydrofluate of molybdic acid with a warm solution of hydrofluate of potash.—2. To obtain the compound free from blue oxide, which is formed with great facility, molybdate of potash is fused with nitre, the mass dissolved in boiling water, and the solution supersaturated with hydrofluoric acid. In both cases, the compound crystallizes on cooling in brilliant, colourless scales, resembling those of boracic acid, and also very like those of the corresponding tungsten compound, only smaller. The crystals are permanent in the air. When heated above 50° or 60°, they lose 6 per cent. of water, assume a greyish-yellow colour, and fuse without further alteration or decomposition to a yellowish-brown mass. When heated with oil of vitriol, they give off hydrofluoric acid, and form at first a splendid blue transparent mass, which afterwards becomes colourless. The crystals dissolve in boiling water and separate again as the liquid cools. (Berzelius.)

	Crystallized.		Berzelius.	Or:		
2K	78·4	26·20	26·27	KO	47·2	15·78
2Mo	96·0	32·08	30·53	MoO^3	72·0	24·06
4F	74·8	25·00		KF	57·9	19·35
4O	32·0	10·70		MoF^3	104·1	34·79
2HO	18·0	6·02	6·00	2HO	18·0	6·02
	299·2	100·00			299·2	100·00

OTHER COMPOUNDS OF MOLYBDENUM.

With manganese, tin, lead, iron, nickel, copper, gold, and platinum, to which metals the molybdenum imparts infusibility, brittleness, and whiteness.

CHAPTER XX.

VANADIUM.

Sefström. *Pogg.* 21, 43; also *Schw.* 62, 316.
Berzelius. *Pogg.* 22, 1; also *Schw.* 62, 323; 63, 26.
Johnston. *N. Edinb. J. of Sc.* 5, 166 & 318; also *Schw.* 63, 119; 64, 88.

SYNONYMES: *Vanad, Vanadin.*

History. Del Rio, in 1801, found that the brown lead-ore of Zimapan consists of oxide of lead and the acid of a metal differing in its characters from chromium; to this metal he gave the name of *Erythronium.* Collet Descotils (*Ann. Chim.* 53, 260) pronounced this metal to be nothing more than chromium, a view which was afterwards adopted by Del Rio himself (*Gilb.* 71, 7), and generally received as true. In 1830, Sefström found that the black powder which remains behind after dissolving the bar-iron obtained from the Taberg ore in hydrochloric acid, contains, besides other substances, a peculiar metal, which he likewise found in still larger quantities in the cinder produced in the conversion of the same iron into wrought iron. To this new metal he gave the name of VANADIUM, from *Vanadis,* a cognomen of the Scandinavian goddess *Freia.* Subsequently, Wöhler proved that the lead-ore of Zimapan consists of vanadiate of lead, and consequently that Del Rio's *Erythronium* is really *Vanadium.* For the more exact investigation of the properties of this metal, we are indebted to Berzelius, from whose writings, excepting where it is otherwise expressly stated, the whole of the following description is taken.

Sources. As vanadiate of lead (Del Rio, *A. Gehl.* 2, 695; Wöhler, *Pogg.* 21, 49; Johnston, *Schw.* 63, 119); as vanadiate of copper (Hess, *J. pr. Chem.* 14, 52); further, in small quantities, in an unknown combination, in the iron-ore of Taberg (Sefström); in the slags of the blast-furnaces of Vordenberg in Steiermark, to the amount of 0·3 per cent. (Schrötter, *Pogg.* 46, 311); in the bog iron ore of Steinlade in Goslar, amounting to less than 0·2 per cent. (Bodemann, *Pogg.* 55, 633); in the bituminous marl slate of Mansfeld, and in the blue slag obtained from it in the reduction of the copper (Kersten, *Pogg.* 51, 539; 53, 385;) in the slag obtained in smelting the bituminous marl slate of Sangerhausen in Thüringen; also in that of Richelsdorf in Kurhessen, especially in the blue and black slags, and less abundantly in the brown or grey varieties; also in the refined copper from the same source (Kersten, *Pogg.* 52, 629); in an iron-ore from Maxen near Pirna, and in the slag and pig-iron obtained from smelting it, at the Frederick-Augustus works (Kersten, *Pogg.* 59, 121); and lately in an iron-slag from Staffordshire, by Deck (*Pharm. Centr.* 1848, 782; *Chem. Gaz.* 1848, 298); in impure pitchblende (Wöhler, *Ann. Pharm.* 41, 345; *Pogg.* 54, 600), apparently as vanadiate of lime, which penetrates the pitchblende in brick-red, highly brilliant, lamellar veins (Ficinus, *J. pr. Chem.* 26, 35); in hydrophite from the Taberg, to the amount of 0·1 per cent. (Lagerhielm, *Jahresber* 20, 216); in vanadic bronzite from Bracco (*vid.* Bronzite, III., 404) to the amount of 34 or per cent. (Schafhäutl.)

Preparation.—1. By exposing vanadic acid in a charcoal crucible to the strongest heat of a blast-furnace. The inner portion of the mass remains in the form of porous suboxide; the exterior only showing traces of reduced vanadium. (Berzelius.) Johnston obtained the metal partly in a coherent state.—2. Fragments of vanadic acid are arranged in layers in a porcelain crucible, with about an equal quantity of potassium, also in small pieces. The cover of the crucible is then fastened down with wire, and the whole heated till rapid reduction takes place, attended with vivid incandescence; the vanadiate of potash is then separated by water from the reduced, pulverulent vanadium.—3. A bulb is blown in the middle of a glass tube, and partly filled with terchloride of vanadium; the terchloride is then saturated with dry ammoniacal gas free from atmospheric air; and the bulb heated by means of an argand spirit-lamp, the stream of ammoniacal gas being still continued. Reduction is instantly effected, the volatile chloride of ammonium being driven off, and the metal left behind in the bulb.

Properties. Vanadium prepared by the first method is reddish-white, like bismuth, difficult to file, brittle, non-magnetic, a good conductor of electricity, and yields a grey powder. (Johnston.) The second method yields it in the form of a heavy black powder, which glitters in sunshine, and when strongly pressed, acquires metallic lustre and the appearance of graphite; it is a good conductor of electricity. When prepared by the third method, vanadium is of an almost silvery whiteness, highly lustrous, brittle, and very easily reduced to powder.

Compounds of Vanadium.

VANADIUM AND OXYGEN.

Vanadium remains unaltered in the air at ordinary temperatures. When heated to incipient redness, it takes fire and burns, though not very vividly, and forms a black infusible oxide. (Berzelius.) The vanadium prepared by the first method becomes incandescent when thus treated, and burns to an indigo-blue oxide at first, then, after long ignition, to vanadic acid. Heated to redness in oxygen gas, it burns with a brilliant red light, and forms indigo-blue oxide, having a crystalline texture. (Johnston.)

The metal, as obtained by the first and third methods, is readily oxidized by nitric and nitro-hydrochloric acids, the product being vanadic oxide, which dissolves in the acid, forming a blue solution. Vanadium is not acted on by water, or even by strong boiling sulphuric, hydrochloric, or hydrofluoric acid, boiling solution of potash, or ignited hydrate or carbonate of potash, provided the air be excluded.

A. SUBOXIDE OF VANADIUM. VO.

Preparation.—1. This oxide is formed by reducing vanadic acid by hydrogen gas, at a red heat. The same substance is obtained whether the vanadic acid is heated just below redness, or to a low or an intense red heat. If vanadic acid in the crystallized state after fusion be used, it retains its crystalline form or texture when converted into the suboxide. —2. By fusing vanadic acid in a charcoal crucible.

As prepared by the first method, it is black, with a semi-metallic lustre, and yields a black powder; the second method yields it in the form of a coherent, very friable mass, having the colour and lustre of graphite. It is infusible, even at the heat of the most powerful blast-furnaces, and a good conductor of electricity.

	Calculation.		Berzelius.
V	68·6	89·56	89·538
O	8·0	10·44	10·462
VO	76·6	100·00	100·000

(VO = 856·89 + 100 = 956·89. Berzelius.)

Decomposed by chlorine gas with the aid of heat, the products being terchloride of vanadium and vanadic acid.

It neither combines with acids nor alkalis, as long as it does not pass to a higher degree of oxidation. Acids, therefore, even at a boiling temperature, do not dissolve it, with the exception of nitric acid. Alkalis dissolve it slowly, inasmuch as it is converted by the action of the air into vanadic oxide. (Berzelius.)

B. VANADIC OXIDE. VANADOUS ACID. VO^2.

Bi-oxide of Vanadium, Vanadinoxyd, Vanadinichte Säure.

Formation. The metal, when heated in the air, burns and forms vanadic oxide at first; the suboxide burns like tinder, and is converted into the black oxide.

Preparation. 1. An intimate mixture of 19 parts (1 atom) of suboxide of vanadium and 23 parts (1 atom) of vanadic acid is heated to whiteness in a current of carbonic acid gas.—2. The hydrate of vanadic oxide is ignited in vacuo. Vanadic oxide may likewise be obtained by igniting vanadiate of ammonia in a retort; but the oxide thus produced is mixed sometimes with suboxide, sometimes with vanadic acid.

Properties. Black and earthy; when prepared by the first method, it forms a solid mass, in consequence of the fusion of the vanadic acid. It does not fuse at the softening point of glass. It is neutral towards vegetable colours.

	Calculation.				Berzelius.
V	68·6	....	81·09	....	81·056
2O	16·0	....	18·91	....	18·944
VO^2	84·6	....	100·00	....	100·000

(VO^2 = 856·89 + 2 . 100 = 1056·89. Berzelius.)

Combinations.—*a.* With water—HYDRATED VANADIC OXIDE.—A salt of vanadic oxide—the sulphate, for example—is precipitated by a very slight excess of carbonate of soda. To insure the absence of vanadic acid, sulphuretted hydrogen must be previously passed through the liquid, and the excess removed by gentle heat; or the solution may be mixed with an excess of acid, and boiled with sugar or alcohol.—The liquid which rests above the greyish white, slowly deposited hydrate, should be perfectly colourless. If it exhibits a blue tint, the carbonate of soda has not been added in sufficient quantity; if it is brown, the precipitant is in too great excess and holds some of the hydrated oxide in solution; a green tint shows that vanadic acid is present. The hydrate is washed out of contact of air, for which purpose the wash-bottle of Berzelius is best adapted, the filter being constantly kept full of water. The water is lastly poured off, and the filter pressed between folds of bibulous paper and dried in vacuo. The hydrate prepared in this way frequently contains a trace of carbonic acid.

Hydrated vanadic oxide is grey; but if it has attracted oxygen during washing, or if it be kept after drying, for a few hours only, in bottles containing air, it acquires a brownish tinge. It is neutral towards blue and red litmus. When left upon moistened litmus paper for some hours, it reddens the paper, because it becomes partially converted into vanadic acid. It is resolved by heat into water and the anhydrous oxide.

b. With Acids, forming the SALTS OF VANADIC OXIDE.—The oxide, after ignition, dissolves perfectly though slowly in acids; the hydrate dissolves more rapidly. The anhydrous salts are brown or green; the hydrated salts either of a dark, medium, or light blue colour. Most of them are soluble in water. The solutions, including those of the basic salts, are of a beautiful blue colour of moderate intensity, and have a sweetish rough taste, exactly like that of ferrous salts. Solutions of vanadic salts, when exposed to the air, frequently become green from oxidation. When mixed with excess of ammonia, the liquid becomes colourless, and a brown precipitate of vanadite of ammonia is formed, which dissolves in pure water, forming a brown solution. With caustic potash or soda, or their simple carbonates, solutions of vanadic salts give a greyish-white precipitate of hydrated oxide, which is dissolved by an excess of the alkali as an alkaline vanadiate, and forms a brown solution, but is again precipitated by a larger excess of the alkali. Alkaline monocarbonates or bicarbonates, produce a greyish white precipitate, soluble in excess of the alkaline bicarbonate, forming a light-blue solution. Hydrosulphate of ammonia throws down a blackish-brown precipitate of bisulphide of vanadium, which dissolves in excess of the precipitant, forming a deep purple solution.—Ferrocyanide of potassium gives a yellow precipitate, which becomes green in the air and is insoluble in acids;—ferricyanide of potassium, a yellowish green gelatinous precipitate. Infusion of galls forms a bluish-black mixture, resembling ink, which, after long standing, deposits black flakes of tannate of vanadic oxide. Hydrosulphuric acid exerts no action on vanadic salts. Zinc does not precipitate any metallic vanadium from the solution.

c. With Salifiable Bases, forming the SALTS OF VANADOUS ACID; VANADITES.—The compounds with the more soluble alkalis are obtained by dissolving the oxide in their solutions; the other salts, which are all insoluble in water, are produced by double decomposition, in the form of pulverulent precipitates.—With the alkaline monocarbonates, vanadic oxide forms a brown solution, which contains a bicarbonate as well as a vanadite of the alkali.—The salts of vanadous acid are dark brown or black.—When moistened or covered with water, or dissolved in it, they assume a green colour, and are rapidly converted by oxidation into salts of vanadic acid, the insoluble salts generally becoming soluble; the dark-brown aqueous solution of the alkaline vanadites is decolorized by this action, the change proceeding from the top to the bottom, and the liquid not turning green. The alkaline vanadites in solution are coloured blue by acids, from formation of double salts; purple-red by hydrosulphuric acid, from production of a bisulphovanadiate of the metal; and blackish-blue by tincture of galls.

Oxides intermediate between Vanadic Oxide and Vanadic Acid.

To be regarded probably as compounds of vanadic oxide with different quantities of vanadic acid.

1. *Purple Oxide of Vanadium.*—When hydrated vanadic oxide, which has been kept for 24 hours in loosely closed bottles containing air, is shaken up with water and filtered, a brownish-green solution of a mixture of the purple and green oxides is obtained. If the hydrate which remains on the filter be washed with a fresh portion of water, it colours the liquid dark-brown; but to a third quantity of water it yields the purple oxide only, giving rise to a fine deep purple solution, which remains unaltered in close vessels, but when exposed to the air becomes first green, and then yellow.—When the hydrate on the filter has ceased to impart any colour to the wash-water, it is merely necessary to expose it to the air for a while, and it will yield the same results with water as before. (Berzelius.)

2. *Green Oxide of Vanadium.* $VO^2, 2VO^3$.—*a.* When the sub-oxide prepared by the first method (p. 82) is exposed to the air, it slowly forms a small quantity of green oxide, the change taking place with greater readiness, the lower the temperature at which the suboxide was produced.

b. An intimate mixture of 1 part (1 atom) of suboxide and 6 parts (5 atoms) of vanadic acid heated to fusion, yields a dark green glass, which, after being reduced to powder, gradually dissolves in water, forming an opaque green solution. $VO+5VO^3=2(VO^2, 2VO^3)$. A similar glass is produced by fusing together 5 parts (one atom) of vanadic oxide with 11 parts (2 atoms) of vanadic acid.

c. When moist hydrated vanadic oxide is left to dry in the open air—whereby it is first turned brown, and afterwards green—then introduced into a small bottle, and the bottle completely filled with water and closed, an opaque green solution is obtained, which, when filtered and evaporated in vacuo over oil of vitriol, yields a black, amorphous, fissured mass, perfectly soluble in water.

d. On mixing aqueous solutions of salts of vanadic oxide free from excess of acid, and of an alkaline vanadiate, a dark green solution is obtained. Thus:

$$VO^2, 2SO^3 + 2(KO, VO^3) = 2(KO, SO^3) + VO^2, 2VO^3.$$

A portion of the green oxide formed, separates if the solutions are at all concentrated, because it is but sparingly soluble in water containing another salt; the rest may therefore be precipitated, for the most part, by the addition of sal-ammoniac. The precipitate is insoluble in absolute alcohol, but dissolves in spirit of specific gravity 0·86. An aqueous solution of the green oxide, diluted sufficiently to render it transparent, exhibits a beautiful grass-green colour.—A small quantity of potash deepens the tint. The solution, if not too dilute, may be evaporated to dryness; whereas when very dilute, it acquires a yellow colour from formation of vanadiate of potash. The residue from the former redissolves in water, forming a green solution, and gives green precipitates with salts of the earths and of the heavy metals. The potash compound may be regarded as a mixture of vanadite and vanadiate of potash.—A larger addition of potash precipitates vanadite of potash from the green solution if the liquid be gently heated, because that salt is insoluble in water containing potash, while vanadiate of potash remains in solution. Ammonia likewise forms a green mixture with an aqueous solution of the green oxide; carbonate of ammonia acts in the same manner; whereas carbonate of potash or soda colour the solution brown, without precipitating it. (Berzelius.)

3. *Yellow-green Oxide of Vanadium.* $VO^2, 4VO^3$.—Formed when a saturated solution of a salt of vanadic oxide is precipitated by an alkaline bivanadiate:

$$e.\,g.\ VO^2, 2SO^3+2(KO, 2VO^3) = 2(KO, SO^3)+VO^2, 4VO^3.$$

The compound when dry, resembles the green oxide; it is, however, more sparingly soluble in water, imparts to it a more yellowish-green colour, and is more completely precipitated from the solution by sal-ammoniac. (Berzelius.)

4. *Orange-yellow Oxide of Vanadium.*—Formed by exposing to the air an aqueous solution of the purple, green, or yellow-green oxide, containing more than one per cent. of oxide. If the oxide is dissolved in a larger quantity of water, it is wholly converted into vanadic acid.

The colour of the liquid passes from green into yellow, and then into orange, and when evaporated at a gentle heat, yields pale orange-yellow crystals, which are soluble in $22\frac{1}{2}$ parts of water, and form an orange-coloured solution. When heated, the crystals give off water and become green. (Berzelius.)

C. VANADIC ACID. VO^3.

Vanadsäure, Vanadinsäure, Acide vanadique.

Formation.—By long continued heating of the metal or of one of its lower oxides in the air; by oxidizing the same substances with nitric acid, aqua-regia, or nitre.

Preparation.—*a. From the cinder of the Taberg iron.*—1. This substance is pounded finely enough to enable it to pass through a hair sieve; and since the iron granules prevent its being more finely pulverized, the powder is first moistened with water in a basin, then digested in nitric acid, warmed, and stirred up till fresh acid no longer produces any oxidizing action. The mixture is then evaporated to dryness, and the residue ignited in an iron pot, after which it is finely pounded, elutriated, and dried on a filter. Three parts of this powder are then intimately mixed with 2 parts of nitre and one part of (dry?) carbonate of soda, by passing the whole three times through a sieve, and the mixture is ignited in a covered cast-iron pot for four hours, at as high a temperature as the vessel will bear. The resulting dense solid mass is then reduced to powder, boiled in a silver vessel with repeated quantities of water, and the solution exactly neutralized with nitric acid, purified by previous boiling from all traces of hyponitric acid, which would reduce the vanadic acid to the state of vanadic oxide. The liquid is then filtered from the precipitated silica (which if it exhibits a brick-red colour, must be freed from the adhering vanadium by digestion in ammonia, and subsequently in boiling water); the filtrate mixed with nitrate or acetate of lead; the resulting precipitate washed, pressed dry, repeatedly agitated with fresh quantities of strong hydrochloric acid; alcohol added; and the mixture heated for some hours nearly to the boiling point of the alcohol, and then thrown on a filter. The blue filtrate contains—besides bichloride of vanadium—phosphoric acid, alumina and zirconia. It is evaporated to dryness in a retort; the residue dissolved in water; and the solution mixed with nitric acid, then saturated with carbonate of potash, again evaporated to dryness, and the residue ignited in a platinum crucible till it is perfectly fixed. The fused mass after cooling is dissolved in the smallest possible quantity of water, and the vanadic acid precipitated in the form of vanadiate of ammonia by the introduction of a large piece of sal-ammoniac into the cold solution. The salt is then washed on a filter with solution of sal-ammoniac, to remove phosphoric acid, afterwards purified from sal-ammoniac by means of alcohol, and lastly ignited in an open vessel to obtain vanadic acid, or in a covered crucible if vanadic oxide is required. (Sefström.)

According to Berzelius, the vanadic acid thus prepared, obstinately retains a portion of silica, which dissolves with it both in acids and in alkalis. To remove this impurity, the vanadic acid is dissolved in oil of vitriol, hydrofluoric acid added, and the mixture evaporated to dryness: by this means fluoride of silicium is first driven off, and then the sulphuric acid.

2. Berzelius ignites the finely powdered cinder with its own weight of nitre and double that quantity of carbonate of soda; exhausts the mass

with boiling water; neutralizes the filtrate with nitric acid; precipitates with chloride of barium or acetate of lead; digests the washed precipitate with oil of vitriol for half an hour; dilutes the red liquid with water; digests the filtrate with alcohol, filters the blue liquid, and evaporates to the consistence of a syrup; then adds hydrofluoric acid, and heats the mixture in a platinum crucible over an open fire, till the whole of the sulphuric acid is expelled (for which a red heat is required); and mixes the remaining vanadic acid with nitre added in small portions at a time, till a sample of the fused mass taken out of the vessel no longer turns red on cooling. He then treats the whole with water; filters from the insoluble compound, consisting of alumina, zirconia, silica, and a small quantity of vanadic acid; washes the latter slightly; and precipitates vanadiate of ammonia from the filtrate by introducing a piece of sal-ammoniac. If the liquid be alkaline, some basic phosphate of ammonia is precipitated at the same time. From the combination with the three earths above mentioned, the vanadic acid may be eliminated by an alkaline bihydrosulphate.

b. From the Mansfeld Copper-Slag.—One part of the slag is reduced to powder and fused in a wrought-iron crucible, with 3 parts of carbonate of soda and 1 part of nitre; the powdered greenish-yellow mass exhausted with boiling water, and the filtrate supersaturated with hydrochloric acid, which turns it green and throws down silica. The whole is then evaporated to dryness, the residue exhausted with pure (not acidulated) water; the filtrate mixed with just enough hydrosulphate of ammonia to precipitate it; the brown precipitate washed, dried, roasted, and then fused with a small quantity of nitre; the mass dissolved in water; the solution neutralised with hydrochloric acid; and lastly, vanadiate of ammonia precipitated by sal-ammoniac. (Kersten, *Pogg.* 51, 539.)

c. From Pitchblende, a mineral containing uranium, vanadium, zinc, lead, iron, cobalt, copper, arsenic, and sulphur. Pulverized pitchblende is fused with its own weight of nitre and carbonate of soda, and the mass exhausted with repeated quantities of boiling water. The filtrate is then exactly neutralized with nitric acid (an excess is immediately discovered by the yellow colour which it imparts to the liquid); precipitated with chloride of barium or acetate of lead; the washed precipitate decomposed by boiling with dilute sulphuric acid; the yellow filtrate, which contains vanadic and likewise arsenic acid, neutralized with ammonia; and vanadiate of ammonia precipitated as before by the introduction of a lump of sal-ammoniac. (Wöhler, *Ann. Pharm.* 41, 345.)

d. From Vanadiate of Lead.—This compound likewise contains hydrochloric acid, phosphoric acid, arsenic acid, and traces of earthy bases. It is dissolved in nitric acid; the lead and arsenic precipitated by sulphuretted hydrogen; the liquid filtered; the blue filtrate boiled for a short time to expel hydrosulphuric acid, and also to precipitate a trace of sulphide of arsenic; the solution evaporated to dryness at a moderate heat; the dark red residue boiled with a perfectly saturated solution of carbonate of ammonia, which is added from time to time; and the liquid filtered boiling hot. On cooling, the vanadiate of ammonia crystallizes out in white needles, which are purified by recrystallization. (Johnston.)

The vanadiate of ammonia is heated, with frequent stirring, in an open crucible to a temperature somewhat below redness, till the black colour of the mass changes to dark red. (Berzelius.)

Properties. The fused acid solidifies on cooling, forming a highly brilliant yellowish-red mass, which is yellowish and translucent at the edges, and consists of acicular crystals with cavities containing aggregations of small crystals. If the acid is mixed with vanadic oxide or any other heavy metallic oxide, it does not crystallize after fusion, but forms a cauliflower-like mass, and appears black; with a small quantity only of vanadic oxide, it may be made to crystallize, but is then of a darker colour, inclining to violet. The powder of vanadic acid is brick-red, or, when finely divided, rusty yellow, the colour being lighter as the powder is finer. Vanadic acid fuses at an incipient red heat, forming a liquid which is yellowish red, according to Sefström, and dark brown, according to Johnston. It then crystallizes on cooling (when it no longer appears red-hot in diffused daylight), and by the heat thereby developed, again becomes ignited, a glowing ring appearing to pass inwards from the circumference to the centre of the mass, where the light continues longest visible. The acid is hereby considerably increased in density, so that it can be easily removed from the crucible. Vanadic acid is not volatile. It does not conduct electricity. It is tasteless, and reddens moistened litmus-paper.

	Calculation.		Berzelius.
V	68·6	74·08	74·045
3O	24·0	25·92	25·955
VO^3	92·6	100·00	100·000

($VO^3 = 856{\cdot}89 + 3 \; . \; 100 = 1156{\cdot}89$. Berzelius.)

Decompositions.—Vanadic acid, when not mixed with carbonaceous substances, may be heated even to whiteness without giving off oxygen. (Berzelius.)—1. When heated with potassium, it is reduced to the metallic state, with vivid incandescence. By exposure to a white heat in contact with charcoal, it is reduced partly to suboxide, and partly to metallic vanadium. (Berzelius, Johnston.) Before the blowpipe, on charcoal, it first fuses, and is then reduced to suboxide having the appearance of graphite; no metal is obtained by the addition of carbonate of soda. (Berzelius.)—2. By hydrogen gas, at a red heat, and even below that temperature, it is reduced to suboxide.—3. When dissolved in water, it is reduced to vanadic oxide; by hydrosulphuric acid, with simultaneous deposition of sulphur; by hydrochloric acid slowly, with disengagement of chlorine; by phosphorous, sulphurous, and hyponitric acids, or fuming nitric acid; by the salts of the lower oxides of many of the heavy metals; and by organic compounds, as oxalic acid, tartaric and citric acid, alcohol, and sugar.—4. Hydrosulphate of ammonia colours the aqueous solution reddish brown.

Combinations.—*a.* With water.—*Solution of Vanadic Acid.*—One part of the acid dissolves in about 1000 parts of boiling water. If the powder is agitated with water, a yellow milk is obtained, from which the undissolved portions of the acid are not deposited till after several days, and without being converted into hydrate. When the yellow, tasteless solution, which is acid to test-paper, is evaporated, it deposits the greater part of the acid in the anhydrous state in red rings round the sides of the basin; ultimately, however, by the reducing action of the dust in the air, a few hydrated crystals of the orange-coloured oxide (p. 85), distinguished by their greater solubility, are produced. (Berzelius.) Hydrosulphuric acid precipitates from the solution a mixture of vanadic oxide and sulphur.

b. With stronger acids.—Vanadic acid readily dissolves in stronger acids, forming yellow or red solutions, which are often rendered colourless by boiling, and yield, on evaporation, red or yellow, partly crystallized compounds, having a powerfully astringent, and subsequently acid taste, resembling that of ferric salts. The acid solutions, if completely saturated with vanadic acid, deposit, on being boiled and evaporated, a brownish red uncrystallizable precipitate containing an excess of vanadic acid. When exposed to the air, the solutions gradually assume a green colour, probably from the reducing action of dust which falls into them. By hydrosulphuric acid, oxalic acid, tartaric acid, alcohol, sugar, &c., they are turned blue, from formation of salts of vanadic oxide. Alkalis produce in them a rusty brown precipitate, which dissolves in excess of the alkali, forming a yellow or brown solution. Hydrosulphate of ammonia gives a brown precipitate of tersulphide of vanadium, soluble in excess of the precipitant, and forming a reddish brown solution. Ferrocyanide of potassium produces a beautiful green precipitate; tincture of galls, after a while, a blackish blue precipitate.

c. With Salifiable Bases, forming Salts called VANADIATES.—The normal salts of this acid are mostly yellow; but those of the alkalis, and of zinc, cadmium, and lead, may likewise be obtained in an isomeric colourless state. This decolorization is produced by heating the solid salt in a watery liquid, or the aqueous solution of that salt, to a temperature just below 100°. It often occurs also at ordinary temperatures, after a longer lapse of time, especially if the solution contains free alkali or alkaline carbonate. The bivanadiates, when in large crystals, exhibit an aurora-red colour; smaller crystals, a yellow tint. The vanadiates have no peculiar taste that can be supposed to proceed from the vanadic acid. They sustain a red heat without alteration, unless the base is volatile or decomposible. Most of them dissolve readily in water, but with less facility in water containing excess of alkali, or sal-ammoniac and other salts; the rest are sparingly soluble; they do not dissolve in alcohol. The aqueous solution is coloured red by the stronger acids, but frequently becomes colourless again after a while. When a mixture of this kind, containing but just enough of the stronger acid to saturate the base, is evaporated, it deposits a red mass, which is a very difficultly soluble acid salt of vanadic acid. If the stronger acid is in excess, the substance which separates is a compound of that acid with excess of vanadic acid. The vanadiates give orange-red precipitates with salts of antimonic oxide, lead-oxide, cupric oxide, and mercuric oxide. With infusion of nut-galls they form, after a while, a mixture as black as ink.

Vanadic acid is insoluble in absolute alcohol, and but sparingly soluble in hydrated alcohol.

D. PERVANADIC ACID?

An aqueous solution of vanadic acid forms a bright red mixture with a solution of peroxide of hydrogen. (Barreswil, *Compt. rend.* 16, 1085.)

Carbonate of vanadic oxide does not appear to exist in the free state, but only in combination with alkaline carbonates.

Vanadium and Boron.

Borate of Vanadic Oxide.—Sulphate of vanadic oxide yields with borax a greyish white precipitate, insoluble in water, but soluble in an aqueous solution of boracic acid, with which it forms a blue liquid, rapidly changing to green when exposed to the air. (Berzelius.)

Vanadium and Phosphorus.

A. **Phosphide of Vanadium.**—Vanadium heated to redness in the vapour of phosphorus, does not combine with it.—By heating phosphate of vanadic oxide to whiteness in a retort with a small portion of sugar, or in a charcoal crucible by itself, a grey porous substance is obtained, which may be compressed into a solid mass having the colour and lustre of graphite.

B. **Phosphate of Vanadic Oxide.**—The blue solution obtained by dissolving vanadic oxide in a slight excess of phosphoric acid, yields, when evaporated at a temperature below 50°, small blue crystals, which may be purified from the colourless mother-liquid—containing nothing but phosphoric acid—by decantation and washing with alcohol. When heated, they leave the anhydrous salt as a white, swollen mass, resembling burnt alum, which, like the crystals, rapidly deliquesces in the air, and forms a thick blue syrup. But if this salt is exposed to a white heat, it fuses imperfectly, and cakes together to a black mass [of pyrophosphate of vanadic oxide?] no longer soluble in water. The crystals deliquesce rapidly in the air. When a concentrated solution of the salt is mixed with anhydrous alcohol, and the resulting precipitate—which is gelatinous, greyish blue, and almost white when dry—is washed with the same liquid, a *salt* is obtained, which is probably *basic*, does not deliquesce in the air, and is but partially soluble in water.

C. **Phosphate of Vanadic Acid.**—*a.* Formed by evaporating a solution of phosphate of vanadic oxide in nitric acid till it turns red and evolves vapours of nitric acid. On slowly cooling the liquid, a lemon-yellow crust is deposited, consisting of small crystallineg rains. The colourless mother-liquid yields, on evaporation, an additional quantity of this compound. It is purified from adhering nitric acid by rinsing with cold water. When its water of crystallization is expelled by heat, it assumes a straw-yellow colour. It dissolves very slowly in water, forming a lemon-yellow solution.

b. By dissolving vanadic acid in phosphoric acid, a red solution is obtained which, on evaporation, yields a red deliquescent mass.

Vanadium and Sulphur.

A. **Bisulphide of Vanadium.**—*Vanadous Sulphide; Sulphovanadous Acid.*—Vanadium does not combine with sulphur when heated in contact with it, or when ignited in its vapour.—1. Suboxide of vanadium is heated to full redness in a current of hydrosulphuric acid gas. In this process, water is formed, and hydrogen gas and even sulphur set free. [Protosulphide of vanadium appears to be the first product, which then absorbs sulphur from the remaining hydrosulphuric acid, till it is converted into bisulphide. At first: $VO+HS=VS+HO$; subsequently: $VS+HS=VS^2+H$.] Vanadic oxide ignited in hydrosulphuric acid gas is first reduced to suboxide with separation of sulphur and formation of water. [$VO^2+HS=VO+HO+S$.]—2. A salt of vanadic oxide is mixed with an alkaline hydrosulphate in excess, till the precipitated sulphide of vanadium is again dissolved: the sulphide is then precipitated by sulphuric or hydrochloric acid. The alkaline hydrosulphate should not contain any excess of sulphur, otherwise tersulphide of vanadium mixes with the precipitate. Bisulphide of vanadium thus precipitated is brown at first, but turns black after being collected into a mass. It may be washed and dried without suffering decomposition.

It is black, and caked together, and when submitted to pressure acquires lustre, but not the metallic lustre: it yields a brown powder.

	Calculation.				Berzelius.
V	68·6	....	68·19	....	68·023
2S	32·0	....	31·81	....	31·977
VS^2	100·6	....	100·00	....	100·000

When heated in the air, it burns with a blue sulphurous flame, leaving a pellicle which is blue at the edges and purple in the centre; after prolonged exposure to heat, fused vanadic acid is obtained. It is converted by nitric or nitro-hydrochloric acid into sulphate of vanadic oxide. It is not affected by hydrochloric or sulphuric acid. That which is prepared by the first method is insoluble in solution of caustic potash or hydrosulphate of potash; but that which is obtained by the second dissolves therein with a purple colour, and in a boiling solution of carbonate of potash, with a brownish yellow colour.

Combinations.—*a.* With Boracic acid.—*b.* With more basic metallic sulphides, forming compounds called SULPHOVANADITES. The soluble compounds with the alkali-metals are obtained either by saturating an alkaline vanadite with hydrosulphuric acid: $KO,VO^2+3HS=KS,VS^2+3HO$, or mixed, either with an alkaline monohydrosulphate, or with some other salt—by dissolving hydrated vanadic oxide in an alkaline byhydrosulphate, or by mixing a salt of vanadic oxide with an alkaline bihydrosulphate.

e.g., $VO^2+2(KS,HS)=KS,VS^2+KS+2HO$;

and: $VO^2,2SO^3+3(KS,HS)=KS,VS^2+2(KO,SO^3)+3HS$.

Hence, when a salt of vanadic oxide is used, half the hydrosulphuric acid is set free, so that an alkaline monohydrosulphate or a metallic protosulphide would suffice. The vanadic salt must be free from excess of vanadic acid, and the alkaline hydrosulphate free from excess of sulphur, to avoid the formation of a compound of tersulphide of vanadium with the alkali-metal.—The insoluble sulphovanadites are obtained by double decomposition.—These compounds in the anhydrous state are black. The sulphovanadites of ammonium, potassium, and sodium, form with water beautiful purple solutions, which resemble the alkaline permanganates, but are rendered turbid by the presence of foreign heavy metallic sulphides. The sulphovanadites of barium, strontium, and calcium are reddish-brown, and but sparingly soluble in water.

B. TERSULPHIDE OF VANADIUM.—*Vanadic Sulphide; Sulphovanadic Acid.*—A solution of vanadic acid in hydrosulphate of ammonia, or an aqueous solution of a vanadiate saturated with hydrosulphuric acid gas is precipitated by an excess of sulphuric or hydrochloric acid.—If too small a quantity of acid is added, a difficultly soluble compound separates, consisting of sulphide of the alkali-metal, with a large excess of tersulphide of vanadium. The precipitate is not decomposed by washing and subsequent drying.

Tersulphide of vanadium, when moist, is of a lighter brown colour than the bisulphide; when dry, it is nearly black, though its powder is liver-coloured.

	Calculation.		Berzelius.
V	68·6	58·83	58·647
3S	48·0	41·17	41·353
VS^3	116·6	100·00	100·000

When heated in a retort it gives off its third atom of sulphur, and leaves bisulphide of vanadium. It is not decomposed by sulphuric acid. It dissolves in caustic alkalis and their carbonates and hydrosulphates, forming reddish brown solutions.

It combines with the more electro-positive metallic sulphides, forming a class of sulphur-salts called SULPHOVANADIATES.

Preparation. 1. An alkaline vanadiate dissolved in water is saturated with hydrosulphuric acid or mixed with bihydrosulphate of ammonia; in the latter case ammonia is set free:

e.g., $KO, VO^3 + 4HS = KS, VS^3 + 4HO$.

2. Vanadic acid is dissolved in an alkaline bihydrosulphate. In this case, the solution likewise contains a protosulphide of the alkali-metal, or an alkaline mono-hydrosulphate:

e.g., $VO^3 + 3(KS, HS) = KS, VS^3 + 2KS + 3HO$.

3. Tersulphide of vanadium is dissolved in a solution of caustic alkali, or of an alkaline carbonate or hydrosulphate. When free alkali or an alkaline carbonate is used, an alkaline vanadiate is doubtless formed at the same time:

e.g., $4VS^3 + 4KO = 3(KS, VS^3) + KO, VO^3$.

4. Substances containing vanadium are fused with carbonate of potash and sulphur. This process, though it yields compounds of less purity than the preceding, serves to separate vanadium from various other compounds.—5. The insoluble sulphovanadiates, those namely, of the earths, and heavy metals, are prepared by precipitating the corresponding soluble compounds with the salt of an earth or heavy metal.

The sulphovanadiates in the dry state are blackish brown. The potassium and sodium salts dissolve readily in water, forming reddish brown solutions; the barium, strontium, and calcium salts dissolve with difficulty; and the rest are totally insoluble. From these solutions, acids in excess precipitate brown tersulphide of vanadium; but a small portion of the sulphide is decomposed at the moment of precipitation by hydrochloric acid (scarcely any by sulphuric acid), so that the liquid appears blue. Alcohol added to an aqueous solution produces a dark-red crystalline precipitate.

C. Sulphate of Vanadic Oxide.—*a. Basic Sulphate.*—Dilute sulphuric acid, or a somewhat concentrated solution of the salt *b*, is completely saturated at a gentle heat, with hydrated vanadic oxide, and the solution evaporated at a slightly elevated temperature, or in vacuo over oil of vitriol. The blue, translucent, amorphous residue, when heated for some time at a temperature of 100°, becomes brown, but continues soluble in water, with which it forms a blue solution. If the solution is allowed to evaporate spontaneously in the air, it turns green, and when further concentrated, deposits a green oxide; the supernatant blue liquid is a concentrated solution of the salt *b*.

b. Bisulphate.—Vanadic acid, or vanadic oxide obtained by igniting vanadiate of ammonia, is dissolved in a warm mixture of equal parts of oil of vitriol and water, and oxalic acid added to the solution as long as carbonic acid is evolved; or the solution is diluted with water—hydrosulphuric acid gas passed through it till the whole of the vanadic acid is reduced to vanadic oxide—and the filtrate evaporated to a small bulk. From the pale blue crystalline crust thus obtained, which is most probably an acid salt, since alcohol removes acid from it, the acid mother-liquor still containing a portion of salt, is decanted; the crust washed several times with alcohol, and then left in contact with alcohol for some time. The salt thus treated swells up, and is converted into a sky-blue bulky powder, consisting of small crystalline scales. This powder is thrown on a filter and washed with absolute alcohol—which acquires a blue colour by dissolving a trace of the salt—and then dried in vacuo, over chloride of calcium or oil of vitriol. In a warm moist atmosphere, the dry salt deliquesces to a syrup; and if this syrup be exposed to the air at ordinary temperatures, it slowly deposits right rhombic prisms, truncated at the acute summits, and having the colour of blue vitriol. The presence of a slight excess of sulphuric acid facilitates the crystallization.

	Anhydrous.			Crystallized.		Berzelius.
VO^2	84·6	51·4	VO^2	84·6	42·17	41·36
$2SO^3$	80·0	48·6	$2SO^3$	80·0	39·88	40·52
			4HO	36·0	17·95	18·12
$VO^2, 2SO^3$	164·6	100·0	+ 4Aq.	200·6	100·00	100·00

The pulverulent salt obtained by the use of alcohol has the same composition as the crystallized salt.

The salt when ignited in a retort yields water, then sulphurous acid, and lastly, anhydrous sulphuric acid, leaving a residue of pure fused vanadic acid. Agitated with water at 10°, it remains suspended, and takes a long time to dissolve, so that even after twelve hours a portion still remains undissolved. It dissolves rapidly in water at 60°, and still more rapidly in boiling water. In warm moist air, it deliquesces more readily than it dissolves in water at 10°. The solution is blue. Absolute alcohol dissolves the salt imperfectly. In alcohol of specific gravity 0·833 it is easily soluble.

D. Sulphate of Vanadic Acid.—*a. Basic Sulphate.*—Formed by boiling a dilute aqueous solution of *c* till it becomes turbid, and collecting the precipitate on a filter.

b. Bisulphate.—$VO^3, 2SO^3$. Formed when a solution of bisulphate of vanadic oxide in nitric acid is evaporated to dryness. Red, deliquescent, saline mass, which dissolves in water, yielding an almost colourless solution.

c. Tersulphate.—$VO^3, 3SO^3$. Vanadic acid is dissolved in a hot mixture of oil of vitriol with half its weight of water, and the excess of sulphuric acid expelled at as low a temperature as possible over the flame of a spirit lamp, the heat being removed as soon as the vapour of sulphuric acid ceases to be evolved. The salt separates in small, red-brown, crystalline scales, which rapidly deliquesce in the air, and form a brownish-red syrup, miscible with water or alcohol, without turbidity; but the aqueous mixture, when boiled, deposits the salt *a*, while the salt *d* remains in solution.

d. Acid Sulphate.—The above-mentioned solution filtered from the salt *a*, leaves a red syrup when evaporated.

E. Borate of Bisulphide of Vanadium.—When hydrosulphuric acid gas is passed through a solution of quadroborate of vanadic oxide, a transparent, dark yellowish brown solution of bisulphide of vanadium in boracic acid is obtained, from which a small quantity of sulphuric acid precipitates the sulphide of vanadium, decolorizing the liquid at the same time. When exposed to the air, it gradually assumes a lighter colour, passing into green, and leaves on evaporation a dark green mixture of green oxide of vanadium, sulphur, and crystallized boracic acid.

Vanadium and Iodine.

Hydrated Biniodide of Vanadium, or Bi-hydriodate of Vanadic Oxide.—Red-hot vanadium does not act on vapour of iodine. The blue solution of vanadic oxide in aqueous hydriodic acid rapidly assumes a green colour when exposed to the air, and when spontaneously evaporated, leaves a brown, semi-fluid mass, which dissolves in water, forming a blackish brown solution, and gives off iodine vapour when treated with oil of vitriol.

Vanadium and Bromine.

Hydrated Bibromide of Vanadium, or Bi-hydrobromate of Vanadic Oxide.—The blue solution of vanadic oxide in aqueous hydrobromic acid turns green during spontaneous evaporation. In vacuo it dries up to a blue gum, which, when gently heated, assumes a violet-brown colour, but still continues almost wholly soluble in water. Alcohol precipitates the compound from the syrupy aqueous solution in the form of a jelly, which again dissolves as the alcohol evaporates.

Vanadium and Chlorine.

A. Aqueous Bichloride of Vanadium, or Bi-hydrochlorate of Vanadic Oxide.—*a. Blue modification.*—Vanadic acid heated with concentrated hydrochloric acid, dissolves as vanadic oxide, with evolution of chlorine. To convert the undissolved portion of the vanadic acid into oxide, and thereby effect its solution, the liquid is digested with metallic vanadium or the sub-oxide, or with sugar or alcohol, or exposed to the action of hydrosulphuric acid gas. The blue solution leaves on evaporation a blue syrup, showing no traces of crystallization; when completely dried at a gentle heat, it gives off hydrochloric acid, and leaves a brown residue chiefly consisting of *basic salt.* A concentrated solution of the bi-acid salt is not precipitated by alcohol.

b. Brown modification.—Vanadic oxide prepared by igniting vanadiate of ammonia in a covered crucible, is dissolved to saturation in concentrated hydrochloric acid. In this case, also, chlorine is disengaged, because the oxide contains vanadic acid mixed with it. The dark brown solution thus obtained does not dry up by spontaneous evaporation, but leaves a black mobile liquid, which again forms a transparent brown solution with water. When evaporated with the aid of heat, it gradually turns blue; and when mixed in a sufficiently concentrated state with a small quantity of sulphuric acid, it is immediately converted into the blue modification without evolution of gas or precipitation.

B. TERCHLORIDE OF VANADIUM.—*Perchloride of Vanadium.*—Vanadium at a red heat burns in chlorine gas, forming a greenish yellow vapour which condenses to a brown red liquid. (Johnston.)—Prepared by passing chlorine gas over a red-hot mixture of suboxide of vanadium and charcoal. To purify the condensed dark yellow liquid from excess of chlorine, atmospheric air dried by chloride of calcium is passed through the apparatus as soon as it is cold, till it no longer smells of chlorine but only of hydrochloric acid. As the air carries along with it small portions of the chloride of vanadium, it is passed into a dilute solution of ammonia to prevent any loss of vanadium.—Terchloride of vanadium is a pale yellow liquid, whose boiling point is above 100°.

	Calculation.		Berzelius.
V	68·6	39·25	
3Cl	106·2	60·75	57·64
VCl^3	174·8	100·00	

Terchloride of vanadium may be boiled over potassium without suffering decomposition; but potassium takes fire when strongly heated in vapour of terchloride of vanadium, forming chloride of potassium and separating the vanadium. In the air, terchloride of vanadium emits a yellowish red cloud, being converted by the moisture present into hydrochloric acid and vanadic acid, the latter of which separates in a finely divided state; it likewise deliquesces rapidly, and forms a dense red liquid covered with vanadic acid: a small quantity of water renders it turbid, by separating a portion of the vanadic acid produced, which likewise contains traces of hydrochloric acid. With a larger quantity of water it forms a transparent, pale yellow solution, having the taste of sesquichloride of iron, which, in a few days, or more rapidly when heated, becomes green and then blue, evolving chlorine and forming bichloride of vanadium, and acts as a solvent on gold. A similar solution is obtained by dissolving vanadic acid in cold concentrated hydrochloric acid. Terchloride of vanadium forms with absolute alcohol a transparent, red mixture, which, however, changes colour more rapidly than the aqueous solution, passing into green and blue, and forming hydrochloric ether. Terchloride of vanadium, when free from water, does not dissolve either vanadium or any other heavy metals. It remains unaltered when its vapour is passed over a red-hot mixture of suboxide of vanadium and charcoal.

Vanadium and Fluorine.

A. Bifluoride of Vanadium, and Bi-hydrofluate of Vanadic Oxide.—The blue solution of vanadic oxide in aqueous hydrofluoric acid, leaves on evaporation a brown mass, perfectly soluble in water; when evaporated spontaneously, it leaves a greenish syrup, from which green crystals are deposited. The crystals dissolve in absolute alcohol, yielding a greenish solution which is turned blue by hydrosulphuric acid. Bifluoride of vanadium combines with the fluorides of potassium and sodium.

B. Ter-fluoride of Vanadium and Ter-hydrofluate of Vanadic oxide.—When a mixture of fluoride of sodium and vanadiate of soda is heated with oil of vitriol, nothing but hydrofluoric acid is disengaged, the vanadic acid remaining with the acid sulphate of soda. Moderately warm hydrofluoric acid readily dissolves vanadic acid, forming a colourless solution, which, if evaporated below 40°, leaves a colourless mass of salt perfectly soluble in water. The salt loses part of its acid when strongly heated, yielding a red mass which still forms a colourless solution with water; at a still higher temperature, the whole of the hydrofluoric acid is expelled, leaving pure vanadic acid.

Vanadium and Nitrogen.

A. Nitrate of Vanadic Oxide.—Vanadium, suboxide of vanadium, or hydrated vanadic oxide, is dissolved in nitric acid. The oxide present in the blue solution thus obtained does not absorb more oxygen from the nitric acid, even at a boiling heat; but when spontaneously evaporated, it becomes green, ultimately decomposing the nitric acid, and drying up to a red mass of vanadic acid, which still retains a portion of the nitric acid.

B. Nitrate of Vanadic Acid.—Dilute nitric acid dissolves a small quantity of vanadic acid; the yellowish solution, when spontaneously evaporated, leaves a reddish mass, from which water still dissolves out a small quantity of nitrate of vanadic acid.

C. Vanadite of Ammonia.—To the gently heated solution of a salt of vanadic oxide, ammonia is added in excess till the precipitate first produced is again dissolved with a blackish brown colour. The solution is then allowed to cool slowly in a well closed vessel. The vanadite of ammonia separates as a brown crystalline powder, leaving the supernatant ammoniacal liquid colourless. The salt dissolves in water, forming a brown solution, and is again precipitated in the form of a brown powder by ammonia. If the aqueous solution is evaporated in vacuo over chloride of calcium, ammonia is evolved, and a brown mass left, which is no longer soluble in water.

D. Hypovanadiate of Ammonia.—A compound of ammonia with vanadous acid and vanadic acid. When a solution of hydrated vanadic oxide in carbonate of ammonia is exposed to the air in a tall narrow cylinder, blackish green, radiating crystals are deposited at the bottom of the vessel. Caustic ammonia, and carbonate of ammonia, added to the green aqueous solution of the green oxide, form a green mixture.

E. Vanadiate of Ammonia.—*a. Monovanadiate.*—*α. White modification.*—1. The reddish yellow solution of bivanadiate of ammonia, prepared by digesting vanadic acid with ammonia in a close vessel, is supersaturated with ammonia, and the yellow mixture warmed till it becomes colourless. The liquid is then left to evaporate spontaneously, or the salt is precipitated by alcohol.—2. A lump of sal-ammoniac, more than sufficient for saturation, is placed in a solution of monovanadiate of potash or soda. The vanadiate of ammonia separates almost entirely from the solution, because it is insoluble in water saturated with sal-ammoniac. The portion which remains dissolved may be precipitated by alcohol, or else as sulphide of vanadium, by mixing it first with an alkaline bihydrosulphate and then with an acid. The white crystalline powder is washed first with a saturated solution of sal-ammoniac, and then with alcohol of 60 per cent.; after which it is dissolved in boiling water containing ammonia, the solution cooled to the crystallizing point, and the salt dried at a temperature between 20° and 30°.

Colourless, translucent, crystalline-granular crust.

The Crystallized salt dried at 60°.			Berzelius.
NH^3	17·0	14·33	
VO^3	92·6	78·08	77.59
HO	9·0	7·59	
NH^4O,VO^3	118·6	100·00	

The salt, when moderately heated, evolves ammonia and becomes lemon-coloured; at a higher temperature, it turns brown; and when heated to redness, evolves ammonia, nitrogen, and water, and leaves vanadiate of vanadic oxide. If strongly ignited in a covered crucible, it leaves a mixture of suboxide of vanadium, vanadic oxide, and vanadiate of vanadic oxide: hence the residue imparts a green colour to water. A boiling solution of ammonia removes the vanadic acid, sulphuric acid dissolves out the vanadic oxide, and the suboxide is left behind. In this case, the liberated ammonia exerts a deoxidizing action on that portion of vanadic acid which first gives up its ammonia and is first heated; for the reduction of the portions of vanadic acid which are last set free and heated, the quantity of ammonia present is insufficient. The salt dissolves very slowly and sparingly in cold water, forming a colourless solution; but in boiling water, it dissolves more quickly, and colours the liquid yellow. The yellow colour does not appear to arise from loss of ammonia; for it is likewise produced when the salt is placed in contact with cold water in a stoppered bottle, and the bottle subsequently immersed in boiling water. The yellow solution is precipitated yellow by sal-ammoniac or alcohol, but becomes colourless on the addition of ammonia; after which, sal-ammoniac throws down a white precipitate. With infusion of galls, the aqueous solution yields a black liquid, which may be used as a nearly insoluble ink.

β. Yellow modification.—The process is the same as in the first method for preparing the white modification—excepting that the yellow solution, instead of being first heated till its colour disappears, is at once left to evaporate spontaneously. Indistinct, lemon-yellow crystals are obtained, which dissolve in water without change of colour, and are again precipitated by alcohol.

b. Bivanadiate.—1. Aqueous ammonia is saturated with vanadic acid in a bottle which is closed and warmed, and the solution left to evaporate. —2. Or better: concentrated acetic acid is added in small quantities at a time, and with frequent stirring, to an almost boiling solution of the simple salt, till the precipitate first formed is redissolved; and the aurora-red solution is left to cool till it crystallizes. The salt forms aurora-red, transparent crystals, soluble in water, from which they are again precipitated by alcohol in the form of a lemon-yellow powder.

c. With excess of acid.—A solution of bivanadiate of ammonia mixed with hydrochloric acid, and evaporated at a temperature between 30° and 40° till it becomes colourless, and afterwards at ordinary temperatures, deposits very small, cubical, brown grains, consisting of a mixture of acid vanadiate of ammonia and basic hydrochlorate of vanadic oxide.

F. CARBONATE OF VANADIC OXIDE AND AMMONIA.—The blue solution of vanadic oxide in excess of bicarbonate of ammonia.

G. BISULPHIDE OF VANADIUM AND HYDROSULPHATE OF AMMONIA.—In the dry state this compound is black; when dissolved, it forms a beautiful purple-red solution.

H. TERSULPHIDE OF VANADIUM + HYDROSULPHATE OF AMMONIA. —A solution of vanadic acid in bihydrosulphate of ammonia rapidly evaporated, deposits a whitish grey mixture of sulphur and sulphovanadiate of ammonium, with excess of tersulphide of vanadium. This precipitate yields, on distillation, water, sulphur, and hydrosulphate of ammonia.

I. BASIC HYDROBROMATE OF VANADIC OXIDE AND AMMONIA.—Thrown down by ammonia from a solution of hydrobromate of vanadic oxide, in the form of a greenish grey precipitate.

K. BASIC HYDROCHLORATE OF VANADIC OXIDE AND AMMONIA.—Ammonia gives with hydrochlorate of vanadic oxide a greenish grey precipitate, insoluble in water.

L. TERCHLORIDE OF VANADIUM + AMMONIA. — Terchloride of vanadium rapidly absorbs ammoniacal gas, with great elevation of temperature, and is converted into a white, uncrystallizable mass, which is partly sublimed by the heat evolved. Heated in a current of ammoniacal gas, it is decomposed, even below redness, into nitrogen gas, water, and metallic vanadium (p. 81, 3).

VANADIUM AND POTASSIUM.

A. VANADITE OF POTASH.—A hot solution of sulphate or hydrochlorate of vanadic oxide is mixed with a slight excess of caustic potash, and the mixture left to cool in a close vessel,—whereupon brilliant, brownish, crystalline scales are deposited, and the colour of the liquid changes from brown to pale yellow. If sulphate of vanadic oxide has been used, the crystals are washed, first with solution of potash, and then with alcohol, and lastly pressed out and dried in vacuo. The salt forms a brown mass having a pearly lustre and permanent in the air. It is very soluble in water, and yields an opaque brown solution. This solution is decolorized by exposure to the air, from formation of vanadiate of potash. An excess of potash precipitates vanadiate of potash from the brown solution, in the form of a brown powder, which redissolves on the application of heat, but again separates for the most part on cooling, so that the liquid retains only a pale yellow colour.

B. HYPOVANADIATE OF POTASH.—See the behaviour of the green oxide with potash (p. 85, *d*).

C. VANADIATE OF POTASH.—*a. Monovanadiate.*—The colourless solution left to evaporate spontaneously, leaves first a syrup, and then a milk-white, earthy mass. Any excess of potash present may be removed by cold water, as the salt itself is difficultly soluble in water, especially if it contains free potash. The salt fuses readily, forming a transparent, yellow liquid, which on cooling solidifies in a white mass. It dissolves slowly in cold but more rapidly in boiling water.—No *yellow modification* of vanadiate of potash is known to exist.

b. Bivanadiate.—1. The salt *a* is fused with vanadic acid in atomic proportions.—2. The salt *a* is boiled with vanadic acid in water.—In both these processes monovanadiate of potash remains mixed with the bivanadiate.—3. Or better: to a nearly boiling aqueous solution of the salt *a*, small portions of strong acetic acid are gradually added, with constant stirring, till the precipitate first formed is redissolved. The liquid is then filtered, if any separation of silica has taken place; the aurora-red solution—which if too dilute must be first concentrated—is mixed with alcohol; the resulting precipitate washed with alcohol, and dissolved in boiling water; and the liquid left to cool till it crystallizes. The crystals are dehydrated by heat.

The anhydrous salt is brick-red; fuses with tolerable facility, and solidifies in a yellow mass on cooling. The crystallized salt appears sometimes in orange-yellow laminæ collected together into a crust, sometimes in lemon-yellow scales having an almost metallic lustre. The crystallized salt dissolves sparingly in cold, but much more abundantly in hot water. In larger quantities of hot water it dissolves without alteration, but a small quantity of hot water dissolves out a mixture of monovanadiate and bivanadiate of potash, leaving a hyper-acid salt undissolved. If the salt is previously fused or dehydrated, the hyper-acid salt is almost always separated on treating it with water. The hot solution as it cools, deposits the greater part of the bivanadiate, while the monovanadiate remains dissolved. When caustic potash is mixed with a hot concentrated solution of bivanadiate of potash, the liquid becomes colourless, and monovanadiate of potash is formed. But if the mixture is made in the cold, the liquid becomes turbid after a certain quantity of potash has been added, and deposits scaly crystals of the bivanadiate, the rest of which may be precipitated by alcohol in the form of a yellow powder. This powder, however, is coloured green by the action of the alcohol, and forms a dark green solution in water; but on evaporating the solution, the characteristic yellow of bivanadiate of potash is again produced.

Anhydrous.			*Crystallized.*			Berzelius.
KO	47·2	20·31	KO	47·2	18·20	89·58
$2VO^3$	185·2	79·69	$2VO^3$	185·2	71·39	
			3HO	27·0	10·41	10·42
$KO,2VO^3$	232·4	100·00	+3Aq	259.4	100·00	100·00

c. *Hyper-acid vanadiate.*—The substance which remains undissolved on treating the salt *b* with a small quantity of hot water.

D. CARBONATE OF VANADIC OXIDE AND POTASH.—Prepared like the corresponding ammonia-salt.

E. SULPHO-VANADITE OF POTASSIUM.—The black compound dissolves in water, yielding a bright purple-red solution.

F. SULPHOVANADIATE OF POTASSIUM.—Separated by alcohol from its reddish-brown aqueous solution, in the form of a scarlet precipitate, which is turned brown by washing with alcohol. When the aqueous solution is evaporated in vacuo, a blackish-brown earthy mass is left which redissolves in water.

G. SULPHATE OF VANADIC OXIDE AND POTASH.—Sulphate of potash dissolved in water is mixed with a slight excess of sulphate of vanadic oxide, the mixture evaporated to a syrupy consistence, and the salt precipitated by alcohol. The precipitate is light blue and very soluble in water. Or, one atom of KO,SO^3 is dissolved in water, together with one atom of $VO^2, 2SO^3$. The solution dries up to a pale blue, opaque, gummy mass, which continues soft for a long time, but at length hardens and exhibits a conchoidal fracture.

H. SULPHATE OF VANADIC ACID AND POTASH.—An aqueous solution of monovanadiate of potash mixed with a small quantity of sulphuric acid and left to evaporate spontaneously, becomes first red, then colourless, and lastly deposits very small acicular crystals collected together into roundish masses, which dissolve very sparingly in water, and are insoluble in alcohol.

I. BIFLUORIDE OF VANADIUM WITH FLUORIDE OF POTASSIUM.—A blue compound, readily soluble in water but insoluble in alcohol.

VANADIUM AND SODIUM.

A. VANADIATE OF SODA.—*a. Monovanadiate.*—Prepared like the potash salt.

b. Bivanadiate.—Large, transparent, aurora-red crystals, which turn yellow in the air from efflorescence, are more soluble in water than the potash salt, and completely precipitated by alcohol from the aqueous solution. Vanadic acid, when fused with carbonate of soda before the blowpipe, sinks into the charcoal.

B. Vanadic acid dissolves in borax in the outer blowpipe flame, forming a yellow bead, which becomes green in the deoxidizing flame,—or, if the bead is tolerably saturated, brownish while hot, and green on cooling. In the outer flame, the green colour is reconverted into yellow; but if the quantity of vanadium is small, it disappears entirely. (This character distinguishes vanadium from chromium.)

C. PHOSPHATE OF VANADIC ACID AND SODA.—An aqueous solution of phosphate of soda and phosphate of vanadic oxide, evaporated with nitric acid at a gentle heat, becomes colourless, and deposits large lemon-yellow grains and lumps, composed of small acicular crystals, which may be purified from the mother-liquor by washing with cold water. The compound dissolves very slowly in water, forming a yellow solution, which does not again yield crystals on evaporation, but dries up to a yellow varnish still soluble in water.

With microcosmic salt, vanadic acid behaves before the blowpipe as with borax.

D. BIFLUORIDE OF VANADIUM + FLUORIDE OF SODIUM.—A blue compound, readily dissolved by water, but insoluble in alcohol.

VANADIUM AND LITHIUM.

VANADIATE OF LITHIA.—*a. Monovanadiate.*—This salt crystallizes out from an aqueous solution evaporated to a syrupy consistence, in small, colourless needles, collected together in dense, rounded masses; it is very soluble in water.

b. Bivanadiate.—Deposited from the yellow, syrupy solution in large, aurora-red crystals, which effloresce in dry air, and are but very imperfectly precipitated from an aqueous solution by alcohol—because the salt, though insoluble in absolute alcohol, dissolves to some extent in ordinary spirit of wine.

VANADIUM AND BARIUM.

A. VANADIATE OF BARYTA.—*a. Basic Vanadiate.*—An aqueous solution of *b* gives with baryta-water, after a while, a yellow precipitate which subsequently becomes white.

b. Monovanadiate.—An aqueous solution of the colourless monovanadiate of ammonia mixed with chloride of barium, rapidly turns yellow, and yields a yellow, gelatinous precipitate, which, at ordinary temperatures, becomes white after a few hours,—but if the mixture is heated, immediately turns white and increases in density. The white and the yellow precipitate have the same composition. When ignited, the salt loses its water of crystallization, and appears yellow while hot and white on cooling. At a full red heat, it fuses to a yellowish brown mass resembling colophony. Before ignition, the salt dissolves sparingly in water, the white variety yielding a colourless, and the yellow variety a yellow solution. The solution, when spontaneously evaporated, deposits small, white, crystalline grains. The salt dissolves in oil of vitriol, forming a red solution.

	Anhydrous.			*Dried at* 60°.			Berzelius.		
BaO	76·6	45·27	BaO	76·6	42·98	42·25	to	43·24
VO^3	92·6	54·73	VO^3	92·6	51·97	50·90	„	51·31
			HO	9·0	5·05	5·79	„	5·56
BaO,VO^3	169·2	100·00	+Aq.	178·2	100·00	98·94	....	100·11

c. Bivanadiate.—The transparent solution obtained on dissolving bivanadiate of potash and chloride of barium in water, deposits, by spontaneous evaporation, short, orange-yellow prisms, or—if mixed with alcohol till it is rendered slightly turbid—brilliant, lemon-yellow scales. The compound is difficultly soluble in water.

B. SULPHOVANADIATE OF BARIUM.—This compound may be obtained in the crystalline form; it is slightly soluble in water, and can therefore be precipitated only from concentrated solutions.

VANADIUM AND STRONTIUM.

A. VANADIATE OF STRONTIA.—*a. Basic Vanadiate.*—Prepared like the baryta-salt.

b. Monovanadiate.—Similar to the baryta-salt, but somewhat more soluble; hence the white crystalline-granular precipitate which monovanadiate of ammonia gives with chloride of strontium, does not appear till after some time. No *yellow vanadiate* of strontia is known to exist.

c. Bivanadiate.—Brilliant, orange-yellow crystals, more soluble than the corresponding baryta-salt.

B. SULPHOVANADIATE OF STRONTIUM.—Resembles the barium compound.

VANADIUM AND CALCIUM.

A. VANADIATE OF LIME.—*a. Basic Vanadiate.*—Prepared in the same manner as the baryta compound; it is, however, more slowly deposited.

b. Monovanadiate.—More soluble even than the strontia-salt; separates in the form of a white or yellowish crust on slowly evaporating the mixed aqueous solutions of monovanadiate of ammonia and chloride of calcium. It is but imperfectly precipitated by alcohol from an aqueous solution.

c. Bivanadiate.—This salt forms large, aurora-red crystals, which do not effloresce but are readily soluble in water.

B. SULPHOVANADIATE OF CALCIUM.—Prepared like the barium compound.

VANADIUM AND MAGNESIUM.

VANADIATE OF MAGNESIA.—*a. Monovanadiate.*—Formed by boiling magnesia alba with vanadic acid and water. The colourless filtrate yields, by spontaneous evaporation in the air, a syrupy liquid, which gradually solidifies to a dense, radiated mass, very soluble in water.

b. Bivanadiate.—An aqueous solution of this salt, when spontaneously evaporated, deposits yellow scales; alcohol precipitates it, though not completely, in the form of a yellow powder. The salt is difficultly soluble in water.

VANADIUM AND YTTRIUM.

VANADIATE OF YTTRIA.—The monovanadiate formed on mixing a salt of yttria with an alkaline monovanadiate, separates in the form of a yellow powder; the bivanadiate produced by using an alkaline bivanadiate remains dissolved.

VANADIUM AND GLUCINUM.

VANADIATE OF GLUCINA.—Both the monovanadiate and bivanadiate of this earth form yellow powders, which dissolve sparingly in water, producing yellow solutions.

Vanadium and Aluminum.

Vanadiate of Alumina.—Resembles the glucina-salt, but is less soluble in water.

Vanadium and Thorinum.

Vanadiate of Thorina.—*a. Monovanadiate.*—Obtained by double decomposition as a yellow precipitate, which is insoluble in water.—*b. Bivanadiate.*—A soluble salt.

Vanadium and Zirconium.

Vanadiate of Zirconia.—Zirconia-salts are coloured yellow by alkaline monovanadiates and bivanadiates, but without precipitation.

Vanadium and Silicium.

A. Silicate of Vanadic Oxide.—Precipitated as a light-grey powder, which, when exposed to the air, assumes first a brown and then a green colour—after which it is no longer soluble in water.

B. Phosphate of Vanadic Acid + Phosphate of Silicic Acid.—Obtained in the preparation of vanadic acid from the cinder of the Taberg iron (p. 86.). It may also be produced by dissolving a mixture of phosphate, silicate, and vanadiate of soda in nitric acid; evaporating the solution till a lemon-yellow, gritty mass is obtained; mixing this with pure water; collecting the pearly scales which appear, on a filter; washing them two or three times with ice-cold water; and pressing them dry between folds of blotting-paper. The compound loses water when heated and assumes a straw-yellow colour. It is readily turned green by deoxidizing substances. It is decomposed by an aqueous solution of carbonate of ammonia, with separation of silica, which, however, retains a portion of the vanadic acid. Water dissolves it with tolerable facility, forming a yellow solution, from which it again separates in crystalline scales on spontaneous evaporation.

	Crystallized.		Berzelius.
$3SiO^2$	93·0	19·58	19·5
$2VO^3$	185·2	39·01	39·0
$2PO^5$	142·8	30·06	30·0
$6HO$	54·0	11·35	11·5
$3SiO^2, PO^5 + 2VO^3, PO^5 + 6Aq.$	475·0	100·00	100·0

Vanadic acid containing silica likewise dissolves completely in sulphuric or hydrochloric acid, without separation of silica.

C. Hydrofluate of Silica and Vanadic Oxide.—*Fluoride of Vanadium and Silicium.*—The blue solution of vanadic oxide in hydrofluosilicic acid leaves, when rapidly evaporated, a blue substance, which, at a moderate heat, swells up to a pale blue porous mass; if allowed to evaporate spontaneously, the solution turns green, and leaves a syrupy liquid containing crystals.

D. HYDROFLUATE OF SILICA AND VANADIC ACID. — *Silicoperfluoride of Vanadium.*—Hydrofluosilicic acid forms a red solution with vanadic acid. By evaporating this solution, an orange-yellow uncrystallizable mass is obtained, which is but partially soluble in water; the solution is pale yellow. The insoluble portion forms a bulky, dark-green mass, which, when treated with oil of vitriol, gives off fluoride of silicium, and dissolves, forming a red solution.

VANADIUM AND TUNGSTEN.

A. TUNGSTATE OF VANADIC OXIDE.—On mixing the concentrated solutions of an alkaline tungstate and a salt of vanadic oxide, a brownish yellow precipitate is formed, which is soluble to a certain extent in water. This substance, when kept under water for a long time, dissolves completely (as the vanadic oxide passes into the state of vanadic acid) and forms a yellow solution.

B. SULPHOTUNSGATE OF VANADIUM.—Sulphate of vanadic oxide yields with sulphotungstate of ammonium a greyish-brown precipitate, which dissolves in water, forming a yellowish-brown solution. This liquid, when exposed to the air, gradually becomes turbid, and yields a deposit chiefly consisting of sulphur.

VANADIUM AND MOLYBDENUM.

MOLYBDATE OF VANADIC OXIDE.—Sulphate of vanadic oxide forms with molybdate of ammonia a dark purple, transparent mixture, which, when exposed to the air, becomes first blue, and then yellow, but does not yield any precipitate. Salts of molybdic oxide form yellow solutions with vanadiate of ammonia.

OTHER COMPOUNDS OF VANADIUM.

With many of the heavy metals, as with platinum. Vanadiates of the heavy metallic oxides heated on charcoal before the blowpipe, readily yield brittle alloys of the reduced metal with vanadium.

CHAPTER XXI.

CHROMIUM.

Vauquelin. *Ann. Chim.* 25, 21, and 194; also *Crell. Ann.* 1798, 1, 183; 1798, 1, 276. Further: *Ann. Chim.* 70, 70.
Richter. *Ueber die n. Gegenst. der Chemie,* 10, 30, and 11, 37. *A. Gehl.* 5, 351.
Godon de St. Menin. *Ann. Chim.* 53, 222.
Mussin-Pouschkin. *Crell. Ann.* 1798, 1, 355, and 2, 444.
John. Chromates. *Schw.* 3, 378.
Berzelius. *Schw.* 22, 53; also *Ann. Chim. Phys.* 17, 7; also *Lehrbuch.* 1826, 2, 55, and 989; also *Pogg.* 1, 34.
Brandenburg. Chromic Acid and Oxides of Chromium. *Schw.* 13, 274. *Scher. Nord. Bl.* 1, 190. *Scher. Nord. Ann.* 1, 297; 2, 126 and 325; 3, 61 and 325; 4, 187.
Döbereiner. Chromic Acid. *Schw.* 22, 476. *N. Tr.* 2, 2, 426.
Meissner. *Gilb.* 60, 366.
Lassaigne. *Ann. Chim. Phys.* 14, 299; also *N. Tr.* 5, 2, 250.
Berthier. *Ann. Chim. Phys.* 17, 56.
Grouvelle. *Ann. Chim. Phys.* 17, 349.
Thomson. Chromate of Potash. *Ann. Phil.* 16, 321.
F. Tassaert. Chromate of Potash. *Ann. Chim. Phys.* 22, 51; also *Schw.* 43, 429; also *N. Tr.* 4, 1, 199,
Moser. *Chemische Abhandlung über das Chrom.* Vienna, 1824.
Otto Unverdorben. Fluoride of Chromium and Chromic Acid. *N. Tr.* 9, 1, 25.
Hayes. *Sill. Amer. J.* 14, 136; 20, 409.
Maus. Chromic Oxide. *Pogg.* 9, 127. Chromic Acid. *Pogg.* 11, 83.
H. Rose. Chloride and Fluoride of Chromium. *Pogg.* 27, 565. Chloride of Chromium. *Pogg.* 45, 183.
Peligot. *Ann. Chim. Phys.* 3, 12, 528.
Moberg. *J. pr. Chem.* 44, 322; abstr. *Ann. Pharm.* 68.
Traube. *Ann. Chim. Phys.* 66, 87, and 165.

SYNONYMES. *Chrom, Chrome.*

History.—Discovered in 1797, by Vauquelin.

Sources.—Not very abundant. As sesquioxide of chromium (*Chrome-ochre*); as sesquioxide of chromium combined with protoxide of iron (*Chrome iron-stone*); as chomate of lead (*Red lead-spar*); also in small quantities in many specimens of meteoric iron; it likewise forms the green or red colouring matter of the emerald, and of diallage, octynolite, greenstone, olivine, fuchsite, pyrosklerite, serpentine, pyrope, and spinelle.

Preparation.—Sesquioxide of chromium (sometimes mixed with one-eighth its weight of lamp-black) is exposed in a charcoal crucible to the most powerful heat of a furnace urged by the bellows. Richter mixed the oxide with one-third its weight of charcoal made from sugar, and reduced it in a luted assay crucible; Berthier exposed it alone in a charcoal crucible for three hours to the heat of a blast-furnace fed with coke; Vauquelin heated chromic acid alone, or sesquichloride of chromium mixed with oil and a small quantity of charcoal (which gave the best result) in a charcoal crucible; Moser mixed 100 parts of sesquioxide of chromium with 22·5 parts of charcoal from sugar, made the mixture into a paste with linseed oil, and exposed it in a porcelain assay crucible to the heat of the pottery-furnace at Vienna. It is very difficult to obtain a solid button of chromium.

Properties.—Colour between tin-white and steel-grey (Richter), whitish grey (Vauquelin). Very brittle, breaking when lightly struck with a hammer. Fracture fine grained (Richter). Texture indistinctly fibrous (Vauquelin). Specific gravity 5·9 (Richter). Fuses with greater difficulty than manganese. Not volatile. Non-magnetic. Berthier obtained this metal in moderately compact, very hard, brittle lumps, steel-grey in some places, black in others. Moser obtained a steel-grey, easily broken mass, composed of four-sided prisms. Gmelin obtained a brittle, metallic, non-magnetic mass, with a dull grey fracture, but interspersed in many places with tin-white crystals.

¶ Berzelius (*Ann. Pharm.* 49, 247) recognises two allotropic modifications of chromium. The first of these, Crα, obtained by reducing sesquichloride of chromium, free from moisture and oxygen, with potassium, is a grey metallic powder, which inflames at a temperature between 200° and 300°, and burns with great splendour, yielding sesquioxide of chromium; it likewise dissolves in hydrochloric acid, with rapid disengagement of hydrogen gas. Crβ, on the contrary, prepared in the ordinary way by reduction with carbon at a high temperature, cannot be oxidized by heat, by boiling in aqua regia, by ignition with potash or nitre, or by hydrofluoric acid. Corresponding modifications may be traced through many of the compounds of chromium.

Atomic weight of Chromium.—26·24 (Peligot); 26·29 (Berlin); 26·79. (Moberg.) ¶

Compounds of Chromium.

CHROMIUM AND OXYGEN.

¶ A. PROTOXIDE OF CHROMIUM OR CHROMOUS OXIDE. CrO.

Probably occurring in *Chrome-iron-ore* and in *Pyrope.* Precipitated in the form of hydrate by the action of potash on a solution of the protochloride. Not known in the free state.

	Calculation.		
Cr	28	....	77·78
O	8	....	22·22
CrO	36	....	100·00

Combinations.—*a.* With Water. Hydrate of Chromous Oxide. *Formation and Preparation.*—When caustic potash is added to a solution of protochloride of chromium (p. 130), a dark brown precipitate of hydrated chromous oxide is obtained. It is very unstable, decomposes water, even at ordinary temperatures, and is converted, almost as soon as it is formed into chromoso-chromic oxide (*q. v.*) with evolution of hydrogen (Peligot). To prevent this decomposition, Moberg (*J. pr. Chem.* 43, 114; 64, 322) proceeds as follows. Protochloride of chromium having been prepared by reducing the sesquichloride in a current of hydrogen gas, the tube in which the reduction is effected is sealed at one end as soon as the action is over, then filled completely with boiled water, and a small tube attached to the other end to carry off the hydrogen which may be evolved by the action of the water on the reduced metallic chromium, which (according to Moberg) is always mixed with the protochloride. The tube is then left to cool, and afterwards inverted in a bottle containing recently boiled solution of potash, and the yellow precipitate of hydrated chromous oxide which immediately separates and falls to the bottom, is washed by means of a siphon arrangement. Lastly, the water is poured off, and the precipitate dried in a sand-bath in a current of hydrogen gas.

Yellow when freshly precipitated; brown when dry. May be preserved unaltered in dry air for three years. When ignited, it gives off hydrogen, and the oxygen thereby separated converts the protoxide of chromium into sesquioxide. (Moberg.)

	Calculation.		Moberg.
CrO	36	80	79·57
HO	9	20	20·43
CrO, HO	45	100	100·00

b. With Salifiable bases: Salts of Chromous Oxide, Chromous Salts.—The hydrated oxide is insoluble in dilute acids, but dissolves slowly in strong acids. The salts are best prepared by mixing a solution of the protochloride with solutions of the corresponding potash or soda-salts, access of air being carefully prevented. They are generally of a red colour, sometimes inclining to blue; but slightly soluble in cold water; more easily in hot water. (Moberg.) Like ferrous salts, they dissolve large quantities of nitric oxide, forming dark brown solutions. Peligot. (For the other reactions, vid. *Protochloride of Chromium*, p. 131.)

¶ B. Chromoso-chromic Oxide. Cr^3O^4.

Peligot's *Deutoxide* or *Oxyde Magnetique.*

According to Peligot, the hydrate of this oxide is formed in greater or smaller quantity, on bringing the protoxide in contact with water (that is to say, at the moment of its precipitation); for, on introducing a solution of the protochloride into a jar filled with mercury, and then passing up a solution of caustic potash, a quantity of hydrogen gas collects at the top as soon as the brown oxide makes its appearance. To complete the decomposition, however, a boiling heat is required. After washing with hot water and drying in vacuo, this oxide has the colour of Spanish tobacco. It is but feebly attacked by acids. When heated it loses water, and is converted into chromic oxide, the change being accompanied by incandescence and evolution of hydrogen, in consequence of the higher oxide being formed at the expense of the water of hydration. From various analyses, Peligot concludes that the hydrate is composed of Cr^3O^4+HO. ¶

C. CHROMIC OXIDE OF SESQUIOXIDE OF CHROMIUM. Cr^2O^3.

Green Oxide of Chromium, Chromgrün.—Formerly also *Chromoxydul, Protoxyde de Chrome.*—Found native in an impure state, as *Chrome-Ochre.*

Formation.—1. At ordinary temperatures chromium remains unaltered in the air, even when moist. (Richter.) When it is heated in moist air, a crust of sesquioxide slowly forms on its surface. (Vauquelin.)—2. Red-hot chromium decomposes a current of aqueous vapour passed over it, hydrogen gas being copiously evolved, and the green oxide formed. (Regnault.)—3. The metal dissolves with great facility in a hot mixture of 1 part of oil of vitriol and 20 parts of water, hydrogen gas being rapidly disengaged. (Regnault, *Ann. Chim. Phys.* 62, 357.) It dissolves in aqueous hydrofluoric acid, especially when heated, hydrogen gas being evolved. (Berzelius.) It dissolves readily in oil of vitriol, with disengagement of hydrogen, and slowly in hydrochloric acid. (Gmelin.)—4. It is dissolved, but very slowly, by hot nitric acid (Vauquelin), or by nitro-hydrochloric acid (Richter).—5. When chromic acid is ignited or treated with deoxidizing substances, sesquioxide of chromium is produced.

Preparation.—I. From *Chrome-iron ore* (a mixture of sesquioxide of chromium and protoxide of iron with magnesia, alumina, and silica).—1. *Preparation of Chromate of potash.*—Vauquelin mixes 2 parts of chrome-iron ore with one part of pure nitre; reduces the mixture to fine powder; ignites it strongly and for a considerable time in an earthen or iron crucible; exhausts the ignited mass with boiling water; and treats the insoluble portion with hydrochloric acid, which dissolves magnesia, alumina, silica, and sesquioxide of iron, and leaves any undecomposed chrome-iron ore behind; this residue is again ignited with one-fourth of its weight of nitre, and exhausted with water. The treatment with nitre and then with water and hydrochloric acid may be repeated till the whole of the mineral is decomposed.—The aqueous solutions (*a*), obtained by exhausting the mass with water, after ignition with nitre, and containing chromate (nitrate, nitrite), silicate, and aluminate of potash, are collected into one, in order to be further treated.—Trommsdorff, (*N. Tr.* 18, 1, 225) uses equal weights of chrome-iron ore and nitre, whereby a more complete decomposition is effected.—Nasse (*Schw.* 43, 339) projects a mixture of 3 parts of chrome-iron ore, 4 parts of nitre, and 2 parts of cream of tartar, by small portions at a time, into a red-hot iron crucible, and exposes the mass, after it has ceased to detonate, to a strong red heat for two hours; he then exhausts it with water, and treats the insoluble residue twice in the same manner, before digesting it with hydrochloric acid. The decomposition is probably more complete in this case than when nitre alone is used. ¶ Jacquelin (*Ann. Chim. Phys.* 21, 478) recommends the use of a lime-salt instead of nitre, and proceeds in the following manner: a pulverized mixture of chrome-iron ore and chalk is ignited, the surface being constantly renewed by stirring; the mass ground down with hot water, and mixed with sulphuric acid till it acquires an acid reaction; and the sesquioxide of iron precipitated by the addition of a small quantity of chalk. In this manner a solution is obtained, consisting of bichromate of lime, contaminated with but a small quantity of sulphate, from which the various salts may be prepared by double decomposition. ¶

2. *Preparation of the Chromic oxide.*—*a.* Vauquelin precipitates the alumina and silica held in solution by the potash, by exactly neutralizing the alkali in liquid (*a*) with nitric acid, the acid being added in small portions at a time till the lemon-yellow colour of the liquid begins to change into reddish yellow: he then filters; evaporates to the crystallizing point; dissolves the resulting crystals of chromate of potash in water; filters; and precipitates chromate of mercurous oxide by adding nitrate of mercurous oxide to the filtrate. The mercury-salt, after being purified with water, and dried, is thoroughly ignited in a porcelain or glass retort; whereupon mercury and oxygen are driven off, and chromic oxide left behind.—Moser omits the neutralizing of the liquid (*a*) with nitric acid, to avoid any admixture of nitre, and endeavours to purify the salt by crystallization alone.—Trommsdorff, (*N. Tr.* 2, I, 366) neutralizes with acetic acid instead of nitric; filters; evaporates to dryness; and removes the acetate of potash by spirit containing 80 per cent, of alcohol.—*b.* Vauquelin mixes the solution (*a*) with excess of sulphuric acid; filters; converts the chromic acid into sesquioxide of chromium by a current of sulphuretted hydrogen gas; precipitates the latter, after filtration, by adding an equivalent quantity of potash (or better, of ammonia); washes the precipitated hydrate, and lastly ignites it.—Nasse converts the chromate of potash into a salt of chromic oxide, by boiling with common salt and sulphuric acid; evaporates the liquid to dryness; dissolves in water; and precipitates the hydrated chromic oxide by supersaturating with an alkali.—*c.* Duflos (*Br. Arch.* 23, 166) passes sulphurous acid gas through the solution (*a*), till the whole of the chromium is precipitated as hydrated sesquioxide. Crystals of pure chromate of potash may first be obtained by evaporating the solution, and the impure mother-liquor afterwards used for the preparation of the hydrated chromic oxide. (Trommsdorff, *N. Tr.* 18, 1, 225.)—*d.* Berzelius adds a boiling solution of pentasulphide of potassium to the boiling liquid (*a*), as long as chromic oxide is thrown down.—In this process the sulphur is oxidized by half the oxygen contained in the chromic acid, and converted into sulphuric acid, which combines with the potash.—*e.* Frick (*Pogg.* 13, 494) boils the liquid (*a*) in a cast-iron pot till it is highly concentrated; then transfers it to glass vessels and leaves it to settle; clarifies the concentrated solution by decantation or filtration; boils it in an iron pot with sulphur till green oxide of chromium ceases to be precipitated; collects the oxide on a filter and washes it; then dissolves it in warm dilute sulphuric acid; filters from sulphur; precipitates chromic oxide from the filtrate by carbonate of soda; and lastly, frees it by ignition from water and carbonic acid. If the washed precipitate is dissolved in hydrochloric acid instead of sulphuric, and the filtrate evaporated to dryness and ignited in an open vessel, an oxide is obtained of a peculiarly splendid green colour. (Liebig.)—*f.* Lassaigne precipitates the earths from the liquid (*a*), by neutralizing with sulphuric acid; evaporates the filtrate to dryness; ignites the residue mixed with an equal weight of sulphur, in a covered crucible; and exhausts the mass with water, which dissolves sulphate of potash and sulphide of potassium, and leaves pure sesquioxide of chromium.—According to Moser, who uses only half the weight of sulphur, the oxide thus

obtained is mixed with sulphur, which may, however, be expelled by repeated ignition in the air.—Wittstein (*Repert.* 66, 65) by igniting for half an hour a mixture of 19 parts of bichromate of potash with 4 parts of sulphur, and washing the residual mass, obtained 9⅓ parts of sesquioxide of chromium.—*g.* Berthier ignites chromate of potash in a charcoal crucible, or mixes it with charcoal powder or lamp-black, and ignites it in an ordinary earthen crucible; dissolves the chromite of potash produced, in cold water; heats the filtrate to the boiling point; collects the precipitated hydrated oxide on a filter; washes it thoroughly with water, and lastly ignites it. The supernatant liquid still contains a portion of chromate of potash, besides carbonate, and, after evaporation to dryness, may be used to decompose fresh portions of chrome-iron ore.—*h.* Wöhler (*Pogg.* 10, 46) ignites a mixture of bichromate of potash with about its own weight of sal-ammoniac and a small quantity of carbonate of soda, in a covered crucible, till no more vapour of sal-ammoniac is disengaged, and then purifies the sesquioxide of chromium from chlorides of potassium and sodium, by washing with water. ¶ *i.* Barian (*Revue sc. & ind.* 20, 425) mixes 4 parts of bichromate of potash with 1 part of starch; ignites the mixture in a crucible, washes away the carbonate of potash with water, and again ignites the residue. He states that the chromic oxide thus obtained is so pure that it may be used for glazing porcelain (provided of course the bichromate be pure in the first instance). *k.* Böttger (*Ann. Pharm.* 47, 339) gives the following method (founded on observations of Unverdorben & Wöhler), of obtaining chromic oxide in the form of unrolled tea leaves. A quantity of crystallized chromic acid, obtained by Warington's method (p. 117), is divided into two equal portions, one portion of which is first neutralized with ammonia, the other then added, and the solution evaporated over oil of vitriol. The bichromate of ammonia crystallizes after a week or two in large cherry-red crystals, which are dried at a gentle heat on bibulous paper. On exposing a small quantity of the salt in a platinum dish, &c. to the flame of a spirit-lamp, a very energetic action takes place, accompanied by strong incandescence, and green bulky masses of chromic oxide shoot out in every direction, very much resembling opened tea leaves.—*l.* According to the same authority, the following method also may be employed. A very fine and intimate mixture is made of 48 parts of gunpowder, 240 parts of perfectly dry bichromate of potash, and 5 parts of equally dry chloride of ammonium. This mixture is made into the shape of a cone (by pressing it into a wine glass, and afterwards carefully shaking it out) and then transferred to an iron plate. A burning fusee or other combustible is then applied to the top of the cone, whereupon it takes fire and burns slowly throughout its whole mass. On exhausting the cone while still hot with water, a residue of chromic oxide is obtained in the form of a pale green powder. ¶

II. *From Red lead spar,* (*Chromate of lead.*)—1. The mineral is reduced to powder and boiled in a mixture of hydrochloric acid and alcohol; the resulting sesquichloride of chromium filtered from the chloride of lead; hydrated chromic oxide precipitated from the solution by ammonia, and then washed and ignited. (Vauquelin.)—2. When native chromate of lead is boiled with a solution of carbonate of potash, the filtered liquid contains chromate of potash mixed with oxide of lead; and from this liquid the oxide of lead is easily separated as an insoluble chromate by treating the solution with a small quantity of nitric acid. (Vauquelin.) From the filtrate containing chromate and carbonate of potash, chromic oxide may be prepared by any of the methods given under I, 1, *a*—*g*. Berthier ignites the native chromate of lead in a charcoal crucible, and frees the resulting chromic oxide from the metallic lead fused with it, partly by means of a sieve, partly by dissolving out the lead with dilute nitric acid.

III. To obtain *crystallized chromic oxide,* a few ounces of chromate of terchloride of chromium are introduced into a small retort of very hard glass, the neck of which is slightly inclined, and reaches, without touching, nearly to the bottom of a flask made of hessian clay, (or into a deep hessian assay crucible, or a wide porcelain tube.) The earthen vessel is then strongly ignited, and the retort heated till the chromate of terchloride of chromium enters into gentle ebullition, and the whole is gradually volatilized. Oxygen and chlorine are evolved and the sesquioxide is deposited on the neck of the retort in crystals which are easily separated in entire crusts. (Wöhler, *Pogg.* 33, 341; also *Ann. Pharm.* 13, 40.) If oil or sal-ammoniac is thrown upon bichromate of potash fused below a red heat, in smaller quantity than that required for decomposing the salt, and the mass heated to whiteness, allowed to cool slowly, and exhausted with water, a mass of green chromic oxide remains, the cavities of which are lined with small, shining, green, and apparently rhombohedral crystals of the same compound. (Ullgren, *Jahresber.* 15, 141.) ¶ If dry chlorine is passed over chromate of potash heated to redness in a porcelain tube, the gas is completely absorbed, giving rise to chloride of potassium and chromic oxide, which, under these circumstances, crystallizes in long brilliant tables. The temperature has a great influence upon the products; thus, at a dull red heat, green friable tables of chromic oxide are obtained; at a strong red heat, on the contrary, brown, very hard crystals, of the same form in other respects, but resembling Wöhler's compound. The crystallization of the chromic oxide is probably promoted by the presence of the chloride of potassium, in the same manner as that of ferric oxide is facilitated, when its sulphate is ignited with common salt. (E. Frémy, *J. Pharm.* 1844, 105, abstr. *Ann. Pharm.* 49, 274.) ¶

Properties.—1. The crystallized chromic oxide obtained by method III., belongs to the rhombohedral system of crystallization. *Fig.* 158, $r^2 : r^3$ *Fig.* 151) = 85° 55′; cleavage distinct parallel to *r:* the crystals are generally macled. (G. Rose.) Sp. gr. = 5·21; scratches quartz, topaz, and hyacinth. (Wöhler.) Of the hardness of corundum. (G. Rose.) Greenish black, with metallic lustre; the powder is also green. (Wöhler.) —2. *Pulverulent* chromic oxide obtained by methods I. or II. *a. After ignition:* bright green, changing to brown every time it is ignited. *b. Obtained by decomposing the hydrate at a temperature below redness:* dark green. Sesquioxide of chromium fuses before the oxyhydrogen blowpipe, and emits a white vapour, but is not reduced to the metallic state. (Clarke.)

	Calculation.		Berzelius.
2Cr	56	70	70·24
3O	24	30	29·76
Cr^2O^3	80	100	100·00

(Cr^2O^3 = 2 . 351·82 + 3 . 100 = 100·364. Berzelius.)

Decompositions.—By charcoal, but only at a most intense white heat; by potassium and sodium at lower temperatures. Not by the oxyhydrogen blowpipe (Clarke); nor by hydrogen gas in a red-hot tube, (Berzelius); nor by carbonic oxide (Göbel Gmelin); nor by sulphur passed in the state of vapour over the white-hot oxide. (Lussaigne.)

Combinations.—a. With Water.—HYDRATED CHROMIC OXIDE. Brandenburg's *pearl-coloured oxide of chromium.* Prepared by precipitating a salt of chromic oxide by ammonia. Also by the methods given under I, 2, *b*, or *c*, and under II, 1, for the preparation of chromic oxide. Bluish-green powder, inclining to grey; green after thorough drying. When pressed out in a moist state between two glass plates, it appears red by transmitted sun-light or candle-light. (Schrötter.) Its colour varies according to the nature of the alkaline precipitant. That which is thrown down by ammonia appears greenish-blue with a tinge of violet, and perfectly violet by candle light; when precipitated by potash, it is green both by day light and candle light. (H. Rose.) [Vid. *Chromite of ammonia.*] At a low red heat it gives off its water, and is converted into the dark green oxide; the latter when strongly heated, begins to glow, and assumes a lighter green colour without further diminution of weight. (Berzelius.) ¶ L. Schaffner, (*Ann. Pharm.* 51, 168), describes three different hydrates of chromic oxide: (1) obtained when sesquichloride of chromium is mixed with excess of potash, and boiled till the supernatant liquid appears colourless, the precipitated hydrate being afterwards washed and dried; (2) prepared by treating the sesquichloride with potash till the precipitate first formed is redissolved, and then adding hydrochloric acid to re-precipitate the hydrated oxide; this variety has a darker colour than that which is precipitated by ammonia; (3) by treating a salt of chromic oxide with excess of ammonia, and drying the resulting hydrate over oil of vitriol. This method yields a hydrate containing nearly 6 atoms of water. According to Frémy, (*Ann. Chim. Phys.* 3, 23, 388), the hydrate obtained by precipitating a salt of chromic oxide by potash, washing with cold water, and drying at ordinary temperatures by a current of dry air, contains 9 atoms of water; whereas the hydrate precipitated by boiling a solution of chromite of potash (p. 144), after being washed from adhering potash and dried as above, contains 8 atoms. The first hydrate dissolves readily in caustic alkalis, the second is completely insoluble.

According to Krüger (*J. pr. Chem.* 32, 383, *Ann. Pharm.* 52, 249), when hydrated chromic oxide is heated in the air, a peculiar change takes place, not hitherto observed, prior to incandescence: viz: the conversion of the sesquioxide into the brown binoxide. (Vid. *Brown oxide of Chromium*, p. 113.) ¶

	Dried at 100°.		Trommsdorff.
Cr^2O^3	80	74·77	74
3HO	27	25·23	26
Cr^2O^3,3HO	107	100·00	100

			Schaffner.
Cr^2O^3	80	68·97	69·24
4HO	36	31·03	30·76
Cr^2O^3,4HO	116	100·00	100·00

			Schaffner.
Cr^2O^3	80	64	64·66
5HO	45	36	35·34
Cr^2O^3,5HO	125	100	100·00

			Frémy.
Cr^2O^3	80	52·63	50·7
8HO	72	47·37	49·3
Cr^2O^3,8HO	152	100·00	100·0

			Frémy.
Cr^2O^3	80	49·68	48·4
9HO	81	50·32	51·6
Cr^2O^3,9HO	161	100·00	100·0

b. With Acids, forming the SALTS OF CHROMIC OXIDE or CHROMIC SALTS. The sesquioxide after ignition is almost wholly insoluble in acids; it dissolves, however, when long boiled in oil of vitriol; the oxide dehydrated at a temperature below redness without having risen to incandescence, is soluble in acids, though it dissolves slowly; the hydrated sesquioxide is easily soluble. The salts of chromic oxide are of a beautiful green or blue colour, and appear red by transmitted light; the soluble salts redden litmus; when they are heated, the acid if volatile, is driven off. Those chromic salts which are insoluble in water, dissolve for the most part in hydrochloric acid. From the aqueous solutions ammonia precipitates the hydrate, a small portion of which redissolves in an excess of the reagent; the stronger the ammonia, the larger is the quantity dissolved. The solution has a peach-blossom colour, even when atmospheric air is completely excluded. Carbonate of ammonia throws down carbonate of chromic oxide which it sparingly redissolves, forming a pale peach-blossom coloured solution. Potash precipitates the hydrate, which readily dissolves at ordinary temperatures in excess of potash, forming a grass-green solution. At the boiling point, however, the hydrate is again completely precipitated, leaving the supernatant liquid colourless. Carbonate of potash throws down a pale green carbonate of the sesquioxide, which dissolves in an excess of the precipitant, though much more sparingly than in caustic potash, forming a solution of a light greenish-blue colour; it is reprecipitated by long boiling. Carbonate of lime also throws down chromic oxide from a cold solution (Fuchs, *Schw.* 62, 191); so likewise do the carbonates of baryta, strontia, and magnesia. (Demarçay, *Ann. Pharm.* 11, 240.) Alkaline hydrosulphates precipitate the green hydrate, with disengagement of hydrosulphuric acid; phosphate of soda precipitates pale green phosphate of chromic oxide; iodide of potassium, whitish-green iodide of chromium, soluble in hydrochloric acid. Chromate of potash added to a perfectly neutral salt of chromic oxide, precipitates yellowish-brown chromate of chromic oxide, which, however, if an excess of acid is present, remains dissolved, forming a yellowish-brown solution, and separates only on the addition of a small quantity of ammonia. Ferrocyanide of potassium produces an emerald-green precipitate, leaving the supernatant liquid strongly coloured. Zinc and iron do not separate metallic chromium from the salts of chromic oxide. These salts are not affected by hydrosulphuric acid, oxalic acid, or ferricyanide of potassium; neither are they precipitated by long boiling with acetate of soda.

c. With some of the alkalis and with protoxide of iron.

Brown Oxide of Chromium, or Chromate of Chromic Oxide.

1. *Insoluble Brown Oxide of Chromium,* or *Neutral Chromate of Chromic Oxide,* CrO^2, or Cr^2O^3, CrO^3?

Formed—1. By the imperfect oxidation of the green oxide by nitric acid or chlorine-water.—2. By the deoxidation of chromic acid, by heating it alone (above 250°), or in contact with hydrated chromic oxide, sulphurous acid, ammonia, and, according to Döbereiner, with organic substances which have no affinity for the sesquioxide, such as paper.

Preparation.—1. Nitrate of chromic oxide is heated till the whole of the nitric acid is decomposed, and then again with a fresh quantity of nitric acid, till the acid is completely expelled, but not quite to redness.

(Vauquelin, Brandenburg.) According to Maus, the nitric acid cannot be completely driven off; inasmuch as, at the temperature required for this purpose, the green oxide is produced.—2. Green hydrated chromic oxide is heated to dryness with an aqueous solution of chromic acid.—3. Hydrated chromic oxide is cautiously heated.—¶ 4. According to Schweitzer (*J. fur Pract. Chem.* 39, 269), when a moderately dilute solution of bichromate of potash is treated with nitric oxide, the gas is absorbed in rather large quantity, the liquid assuming a dark colour, and after some time depositing a brown precipitate. This substance has all the properties of brown oxide of chromium. ¶

Dark brown, somewhat shining powder (Vauquelin): lemon-yellow powder (Brandenburg).

At a temperature just below redness, it gives off oxygen gas, and is converted into the ordinary green oxide; when treated with hydrochloric acid, it yields chlorine gas and green hydrochlorate of chromic oxide. (Berzelius.) A warm solution of oxalic, tartaric, citric, or acetic acid, likewise dissolves it in the state of green oxide, with separation of oxygen gas. (Brandenburg.)

¶ Krüger maintains that this brown substance (at least as prepared according to 3) is really a binoxide of chromium, and not a compound of chromic oxide and chromic acid, because it yields only chlorine and no chromate of sesquichloride of chromium, when heated with common salt and sulphuric acid [or with hydrochloric acid?] *vid.* p. 115. ¶

Combinations.—*a.* With water: *Hydrated Brown Oxide of Chromium.*—1. Nitrate of chromic oxide is heated till the nitric acid is partially decomposed. The mass is then dissolved in water, and the hydrate precipitated from the brownish red solution by excess of ammonia. (Vauquelin.) By this process, Moser obtained the hydrated green oxide, but of a somewhat darker colour than usual.—2. Chlorine gas is passed through the solution of a salt of chromic oxide while it is being precipitated with potash. (Vauquelin.) This method did not succeed in Moser's hands.—3. Sulphurous acid is passed into an aqueous solution of chromic acid; and from the resulting brown solution, the brown hydrate is precipitated by ammonia. (Vauquelin.)—4. The hydrated brown oxide is likewise precipitated by boiling a solution of chromate of ammonia. (Vauquelin.)—5. Through a mixture of the solutions of chromate and carbonate of potash, a mixture of nitrous gas and atmospheric air (nitrous acid vapour) is passed, and the hydrate is precipitated by heating the mixture to the boiling point; if too much nitrous acid is used, nothing but nitrate of the protoxide is formed. (Grouvelle.)—6. A mixture of chromate of potash, nitrate of ammonia, and carbonate of potash, is evaporated to dryness, gently heated till the mass turns black, and then digested in water: the portion of oxide which redissolves is afterwards precipitated by ammonia. (Grouvelle.)—7. The hydrated green oxide is digested with an aqueous solution of chromic acid, the latter not being in excess. (Maus.)—8. Hydrochloric acid is thoroughly saturated with green oxide of chromium, and precipitated by monochromate of potash. (Maus.)—Bensch (*Pogg.* 55, 98) uses for this purpose a boiling solution of sulphate of chromic oxide.

The hydrate, when moist, is reddish brown; when dry, it is black (Vauquelin), or dirty yellow (Bensch).

b. With acids, forming the *Salts of Brown Oxide of Chromium.* The strongly heated oxide is dissolved by acids with great difficulty; the hydrate, readily, forming a brown solution. The solution reddens litmus, and is precipitated by ammonia in large brown flakes; but if the ammonia is in excess, the brown oxide is resolved into green oxide and chromic acid, which combines with the ammonia. The solution does not precipitate the salts of lead, mercury, or silver.

c. With the alkalis in solution, especially with potash.

The supposition of John and Döbereiner, that brown oxide of chromium is not a distinct compound of chromium and oxygen, but merely a very feeble compound of the green oxide with chromic acid, is rendered highly probable by the following experiments of Maus: When the hydrated brown oxide is washed with cold water, the process must be continued for three weeks before the wash-water (containing chromic oxide with excess of chromic acid) ceases to affect a salt of lead; the washed residue is then found to be converted into hydrated green oxide. Hot water acts in the same manner, but much more rapidly. A solution of sal-ammoniac or alcohol acts like water.—The hydrated brown oxide digested with acetate of lead is converted into chromate of lead, while the supernatant liquid contains acetate of the green oxide; a slight excess of acetic acid accelerates the decomposition.—By digestion with small quantities of arsenic acid in solution, the brown hydrate is converted into insoluble arseniate of green chromic oxide (which would dissolve were the arsenic acid present in excess), and the solution contains pure chromic acid.

¶ 2. *Bichromate of Chromic Oxide.*

$Cr^2O^3, 2CrO^3$ or Cr^4O^9.

1. When chromic acid is exposed on a glass plate, it dries up to a brown crust which is insoluble in water, and adheres strongly to the glass. This substance is bichromate of chromic oxide, produced by the action of the dust in the air. It may also be prepared by treating a moderately dilute solution of chromic acid with excess of alcohol at ordinary temperatures, and heating the mixture after the evolution of aldehyde has ceased: in a short time the reduction is complete. Part of the compound sinks to the bottom of the vessel; part remains suspended in the liquid, even after some weeks. The precipitate is boiled with water till the smell of pure acetic acid is apparent, then agitated with water, and lastly with absolute alcohol, till nothing more is dissolved out by either liquid. The pure salt, when dry, presents the appearance of a brittle, fissured mass, and yields a greenish-brown powder. Before drying, it is readily soluble in hydrochloric and nitric acid, and with greater difficulty in acetic acid. From these solutions chromic oxide is precipitated by ammonia. Caustic potash easily dissolves it. (Traube.)—2. When a solution of chrome-alum is mixed with a solution of neutral chromate of potash, the mixture first becomes brownish red, and subsequently deposits a bright brown precipitate, the supernatant liquid having an intense yellow colour. The precipitate is washed with cold water till it passes through the filter colourless. This compound dissolves in hydrochloric acid with a yellowish green, and in nitric acid with a brown colour; the solution in both cases yields with ammonia a precipitate of chromic oxide, leaving chromic acid in solution. Dilute sulphuric acid slowly dissolves it at a boiling heat, forming a brown liquid. Solution of potash rapidly resolves it into chromic oxide and chromic acid; ammonia does not affect it.

3. *Neutral Chromate of Chromic Oxide.*

$Cr^2O^3, 3CrO^3$.

This substance is formed, according to Traube, when chromic acid is heated above 250°. By boiling with water, or after remaining for a long time in contact with that liquid, it is converted into a soluble modification of the same salt, imparting to the water in the first case a yellowish, and in the second a deep brown colour. When it is heated with hydrochloric acid, chlorine is evolved, and a solution of sesquichloride of chromium obtained; nitric acid dissolves it very slowly. Dilute sulphuric acid slowly resolves it into soluble sulphate of chromic oxide and chromic acid; concentrated sulphuric acid, on the contrary, aided by heat, forms with it an insoluble sulphate of chromic oxide and chromic acid. Potash decomposes it readily; ammonia with difficulty, the action being apparently due to the water contained in the ammonia. The salt contains 57·93 per cent. of chromium, and 42·07 of oxygen. (Traube.) ¶

4. *Soluble Brown Chromic Oxide or Acid Chromate of Chromic Acid.*

Cr^2O^5 or $Cr^2O^3, 4CrO^3$.

1. A cold aqueous solution of chromic acid rapidly dissolves the hydrate or carbonate of green chromic oxide. The solution has a darker brown colour than pure chromic acid; is not rendered turbid by boiling; and leaves, on evaporation, a brittle horny mass, which is permanent in the air, and dissolves without change in cold alcohol. It contains 27·79 per cent. (1 atom) of the green oxide, and 72·21 per cent. (4 atoms) of chromic acid. (Maus.) The solution gives a green precipitate with ammonia; it may be repeatedly evaporated to dryness at a temperature of 100°, without being decomposed; but if the evaporated mass is kept at that temperature for a long time, it becomes insoluble. (Hayes.) On mixing green sesquichloride of chromium with monochromate of potash, a green solution is first obtained, which turns brown, and then deposits a precipitate of the first compound; the liquid, however, still remains brown. Possibly it contains the fourth compound $= Cr^2O^5$, and the precipitate should be regarded as CrO^2. (Berzelius.) [Probably then in this manner: $Cr^2O^3, 3HCl + 3(KO, CrO^3) = 3(KO, HCl) + 2(Cr^2O^5) + CrO^2$].

C. Chromic Acid. CrO^3.

Chromsäure, Acide chromique.

Formation.—1. By igniting chromic oxide with potash in an open vessel, or with nitre, chlorate of potash (which rapidly disengages chlorine gas), or peroxide of lead, the product being chromate of potash, or chromate of lead.—2. By treating the hydrated sesquioxide with an aqueous solution of hypochlorous acid. (Balard.)

Preparation.—1. A mixture of 1 part of chromate of lead, 1 part of fluorspar, and 3 parts of fuming oil of vitriol, is gently heated in a leaden vessel, over which a larger vessel of the same material, perforated with a great number of holes for the admission of air, is inverted. The terfluoride of chromium ascending in vapour is decomposed by the moisture of the air into volatile hydrofluoric acid and solid chromic acid, which is prevented from falling into the lower vessel by a perforated leaden plate laid on the mouth. (Unverdorben.) The further purification recommended by Unverdorben, which consists in precipitating with nitrate of silver and decomposing the chromate of silver by hydrochloric acid, will probably yield a chromic acid containing hydrochloric or nitric acid. A considerable quantity of chromium remains behind in the leaden vessel, because the water in the oil of vitriol prevents, to a certain extent, the formation of fluoride of chromium; anhydrous sulphuric acid, or even fuming oil of vitriol, is not adapted to the purpose, because the anhydrous acid volatilizes with the fluoride of chromium. (Maus).—2. A mixture of 4 parts of chromate of lead (or 3·2 parts of chromate of baryta), 3 parts of fluorspar free from silica, and 5 parts of fuming sulphuric acid, or English oil of vitriol freed by boiling from excess of water, is gently heated in a leaden, or better in a platinum retort, over an oil lamp; the vapour of fluoride of chromium thereby evolved is passed into a platinum receiver containing water; and the hydrofluoric acid and water expelled by evaporation (the addition of powdered quartz is quite unnecessary): the residue consists of chromic acid. (Berzelius.)—3. A hot solution of bichromate of potash is mixed with a quantity of hydrofluosilicic acid, not quite sufficient for precipitating the whole of the potash; the solution filtered from the double fluoride of silicium and potassium; the latter washed with water; the filtrate evaporated to a small bulk in a porcelain basin; the remainder of the potash precipitated by a slight excess of hydrofluosilicic acid; the liquid evaporated to dryness in a platinum dish (a vessel of porcelain would be attacked by the excess of hydrofluosilicic acid); the residue dissolved in the smallest possible quantity of water; the aqueous solution of chromic acid decanted (a filter would be destroyed by so concentrated a solution) from double fluoride of silicium and potassium; and lastly, evaporated to dryness. (Maus.)—4. A warm solution of bichromate of potash is carefully added to an excess of oil of vitriol (any excess of the salt would crystallize out without being decomposed, and thus contaminate the chromic acid); the liquid poured off from the chromic acid, which separates in small red crystals; and the crystals drained in a funnel having its stem partly filled with coarsely pounded glass. The chromic acid is then placed under an evaporating jar, on a brick which absorbs more of the sulphuric acid; and lastly dissolved in a small quantity of boiling water. On cooling, the solution deposits crystals of nearly pure chromic acid. (Fritzsche.) Warington (*J. pr. Chem.* 27, 252) mixes 10 measures of a cold saturated solution of bichromate of potash with from 12 to 15 measures of oil of vitriol, free from lead, and presses the red acicular crystals, which separate as the liquid cools, between porous stones. The chromic acid thus prepared contains but a trace of sulphuric acid. ¶ Bolley (*Ann. Pharm.* 56, 113) improves upon this method by dissolving a weighed quantity of bichromate of potash in a small quantity of boiling water, and adding to the hot solution the exact quantity of ordinary sulphuric acid required to convert the potash into bisulphate. The mixture is then left to cool, whereupon it solidifies for the most part in a red granular mass, consisting of bisulphate of potash with adhering chromic acid. The mixture is stirred to separate the insoluble grains, and the solution decanted from the bisulphate of potash, which is washed several times with cold water to remove the whole of the chromic acid. The solution of chromic acid containing a small quantity of bisulphate of potash is then further concentrated, and the chromic acid precipitated by about an equal volume of sulphuric acid, which throws it down free from all traces of bisulphate of potash. It is then drained in a glass funnel, loosely closed with pieces of glass, and finally obtained in perfectly pure and large crystals by repeated solution in water, and recrystallization by slow evaporation.—Traube (*Ann. Pharm.* 66, 170) heats 1 part of bichromate of potash with 3½ parts of sulphuric acid and 2½ parts of water, and adds 4 parts of sulphuric acid to the solution of chromic acid decanted from the crystallized bisulphate of potash. The chromic acid is precipitated in red flakes, which are redissolved in a small quantity of water, and the solution evaporated to the crystallizing point. The acid thus obtained may be purified from chromate of potash either by re-solution in water and precipitation by sulphuric acid, &c., or by careful fusion in an air-bath, whereby insoluble double sulphate of chromic oxide and potash, and insoluble sulphate of chromic oxide are obtained by the mutual action of the several elements present. The chromic acid is afterwards separated by exhausting with cold water, and crystallized by evaporation in the ordinary way. ¶—5. Chromate of baryta is digested with a quantity of dilute sulphuric acid, not sufficient for complete saturation, and the baryta precipitated from the filtrate—which contains chromic acid and acid chromate of baryta—by the exact amount of sulphuric acid required, so that the solution is neither affected by sulphuric acid nor by a salt of baryta; it is then filtered and evaporated to dryness. (Meissner.)—Döbereiner decomposes chromate of baryta with a slight excess of sulphuric acid, and afterwards removes the excess of sulphuric acid from the filtrate by the addition of an equivalent quantity of baryta-water.

Properties.—As prepared by the first method, chromic acid forms a delicate, woolly, scarlet-coloured, asbestos-like mass, so light that a cubic inch weighs only 0·2 of a gramme. (Unverdorben.) Prepared by the second method, it forms a solid, dark red mass, which turns black when heated. (Berzelius.) From a concentrated solution, it crystallizes in carmine-coloured needles, or in large brownish red crystals which yield a carmine-coloured powder. (Fritzsche.) It fuses when heated [to 180° or 190° *Traube*], forming a bright reddish brown liquid, which, on cooling, solidifies in a red, opaque, and brittle mass. (Unverdorben.) Chromic acid is inodorous; tastes very acid at first, and afterwards rough, but not metallic; it imparts to the skin a yellow stain, which is not removed by water but yields to an alkali. (Unverdorben, Berzelius.)

	Calculation.				Berzelius.
Cr	28	...	53·85	...	54·13
3O	24	...	46·15	...	45·87
CrO^3	52	...	100·00	...	100·00

Or:

					Godon.		Vauquelin.
Cr^2O^3	80	...	76·9	...	74·1	...	85·8
3O	24	...	23·1	...	25·9	...	14·2
$2CrO^3$	104	...	100·0	..	100·0	...	100·0

($CrO^3 = 351·32 + 3 . 100 = 651·82$. Berzelius.)

Decompositions.—When heated above the melting point [above 250°, *Traube*], it is resolved into oxygen gas and sesquioxide of chromium [neutral chromate of chromic oxide, *Traube*], and if the acid has been prepared by the first method, the resulting oxide exhibits incandescence. (Unverdorben, Berzelius.) By heating the acid with oil of vitriol, oxygen gas and sulphate of chromic oxide, are obtained.—2. If chromic acid, prepared by the second method, be introduced at ordinary temperatures into ammoniacal gas, it instantly becomes white hot, and is reduced into chromic oxide. (Unverdorben, Böttger, *Ann. Pharm.* 57, 134.)—3. Heated potassium or sodium reduces chromic acid with incandescence—probably to the metallic state. (Gay-Lussac & Thénard.)—4. Phosphorus dissolves in an aqueous solution of chromic acid, producing green phosphate of chromic oxide. (Jacobson.)—5. When hydrosulphuric acid gas is passed over the dry heated acid, decomposition takes place, attended with vivid incandescence, the products being sulphur, water, and sesquisulphide of chromium. (Harten, *Ann. Pharm.* 37, 350.)

$$2CrO^3 + 6HS = Cr^2S^3 + 6HO + 3S.$$

The aqueous acid is decomposed by sulphuretted hydrogen into water, sulphur, and chromic oxide. — 6. Sulphurous acid converts aqueous chromic acid into sulphate of chromic oxide.

$$2CrO^3 + 3SO^2 = Cr^2O^3, 3SO^3.$$

With a smaller quantity of sulphurous acid, the brown oxide of chromium is produced. ¶ Dry chromic acid is not affected by sulphurous acid at 100°; at 180° that acid converts it into chromate of chromic oxide, with evolution of anhydrous sulphuric acid. (Traube, *Ann. Pharm.* 66, 103.)—7. Hydriodic acid and boiling hydrochloric acid form green solutions of sesquiodide or sesquichloride of chromium, with evolution of iodine or chlorine.—8. Chromic acid in solution is likewise reduced to the state of chromic oxide by nitric oxide, by arsenious acid, and by agitation with mercury.—9. Many organic substances, as citric acid, tartaric acid, alcohol, and paper, convert chromic acid, especially when aided by light, or heat, into green or brown oxide, carbonic acid being formed at the same time. The concentrated acid corrodes paper like oil of vitriol, the action being attended with formation of brown oxide of chromium. (Maus.) The dilute acid assumes a green colour when exposed to light. Vegetable substances saturated with aqueous chromic acid and then dried, burn with a vivid and continuous flame. (Jacobson.)

Combinations.—*a.* With Water.—*Aqueous Chromic Acid.*—Chromic acid rapidly deliquesces in the air, and dissolves very easily in water, forming a dark reddish brown, or, with more water, a lemon-yellow solution. Chromic acid imparts a yellow colour to very large quantities of water.

b. With Salifiable Bases, chromic acid forms salts called CHROMATES. Most of them are either bibasic, monobasic, or biacid salts. The normal chromates of the alkalis and earths are yellow; the alkaline bichromates, aurora-red; the chromates of the heavy metals are bright yellow, red, or occasionally of some other colour. The alkaline monochromates remain undecomposed even at a full red heat, unless carbon is present, in which case the chromic acid is reduced to chromic oxide; chromates containing a weaker base give off oxygen gas when heated alone, and form chromic oxide. Before the blowpipe, the chromates impart a green colour to borax and microcosmic salt. When heated with oil of vitriol, they all evolve oxygen gas, and yield sulphate of chromic oxide, together with another sulphate. The anhydrous salts, heated with hydrochloric acid, evolve chlorine gas, and form sesquichloride of chromium and another metallic chloride. Heated in the anhydrous state with common salt and oil of vitriol, they give off red vapours of chlorochromic acid, which condenses to a brownish red liquid. Similarly, when heated with fluorspar and oil of vitriol, they evolve red vapours of terfluoride of chromium. A few only of the chromates, more particularly those of the alkalis, are soluble in water, but they all dissolve in nitric acid. ¶ Kopp has obtained many of the heavy metallic chromates in a hydrated and even soluble form, by digesting the corresponding metallic sulphate with chromate of baryta for a considerable time, or more rapidly by treating the oxide or carbonate with a dilute solution of chromic acid. The salts thus obtained are precisely analogous to the corresponding sulphates (vid. *chromate of copper* and *chromate of zinc*). ¶ The aqueous yellow solutions (reddish yellow, if they contain excess of chromic acid) assume a deeper colour on the addition of sulphuric, nitric, or hydrochloric acid, in consequence of the separation of chromic acid. When hydrochloric acid is used, chlorine is evolved, and the red colour changes to the green of sesquichloride of chromium, gradually at ordinary temperatures, more quickly on boiling, and still more quickly on the addition of alcohol. When the solution of a chromate is mixed with sulphuric or acetic acid, and a current of hydrosulphuric acid gas passed through it, sulphur is deposited and the liquid assumes a green colour from formation of sulphate or acetate of chromic oxide. According to H. Rose, the whole of the sulphur in the hydrosulphuric acid is precipitated in the free state, but if the gas is passed through a hot mixture of a chromate with acetic acid, decomposition is more rapidly effected, and the greater part of the sulphur is converted into sulphuric acid. Sulphurous acid rapidly converts chromic acid in the soluble salts into sulphate of chromic oxide. Zinc decomposes the alkaline monochromates and bichromates, when dissolved in water and mixed with sulphuric acid, forming a green solution of chromic sulphate. Mercury, according to Jacobson (*J. pr. Chem.* 23, 467), quickly produces in solutions of the alkaline bichromates, and more slowly in solutions of the monochromates, a precipitate of hydrated chromic oxide. Oxalic, tartaric, or citric acid (but not acetic acid), converts the soluble chromates, especially when heated, into green solutions of chromic oxide, with evolution of carbonic acid. Alcohol and sugar act in a similar manner, on the addition of a small quantity of sulphuric acid. The alkaline chromates, dissolved in water, precipitate baryta salts pale yellow, lead and bismuth salts bright yellow, mercurous salts brick red, and silver salts purple red; these precipitates are all soluble in nitric acid.

c. With several metallic chlorides, which play the part of a basic metallic oxide.

d. Chromic acid is soluble in alcohol and ether.

D. PERCHROMIC ACID. Cr^2O^7.

Ueberchromsäure, Acide surchromique.

When peroxide of hydrogen, dissolved in water, is mixed with a solution of chromic acid, the liquid assumes a deep indigo-blue colour; but it often loses this colour very rapidly, the liquid evolving oxygen gas, The same blue colour is likewise produced on adding a mixture of aqueous peroxide of hydrogen and sulphuric acid, or hydrochloric acid, to bichromate of potash; but in a very short time oxygen gas is disengaged and a potash salt together with a chromic salt, is left in the solution. In this case, for each atom of bichromate of potash, 4 atoms of oxygen gas are evolved, provided an excess of peroxide of hydrogen is present:

$$KO, 2CrO^3 + O + 4SO^3 = KO, SO^3 + Cr^2O^3, 3SO^3 + 4O.$$

Consequently, the peroxide of hydrogen must first have given up one atom of O to the two atoms of CrO^3 and formed Cr^2O^7, this compound being subsequently resolved, with evolution of four atoms of O, into Cr^2O^3. With ether, the acid forms a more stable blue mixture than with water. To prepare this compound, according to Thénard's directions (p. 74), peroxide of barium is dissolved in hydrochloric acid; the liquid covered with a stratum of ether; a solution of bichromate of potash carefully added, and the whole agitated together: the lower aqueous stratum then appears colourless, and the blue ethereal solution is poured off. When the liquid is left to evaporate in the air, the whole of the ether escapes, but the blue colour suddenly disappears, with evolution of oxygen gas, and chromic acid alone remains. Alkalis instantly decompose perchromic acid, disengaging oxygen gas and forming an alkaline chromate. Perchromic acid, however, dissolved in ether, may be made to unite with ammonia and certain organic bases, producing very stable compounds, from which stronger acids separate the blue acid. (Barreswil, *Compt. rend.* 16, 1085; also *J. pr. Chem.* 29, 296; also *Instit.* 1846, 320.)

CHROMIUM AND CARBON.

¶ CARBONATE OF CHROMOUS OXIDE.—The precipitate produced in a solution of protochloride of chromium by alkaline carbonates resembles in many respects the carbonates of magnesia, zinc, and ferrous oxide.—1. When the protochloride is added to a boiling solution of carbonate of potash, a red or reddish brown precipitate is formed, which, when the ebullition ceases, gradually acquires a bluish green colour (provided air be excluded), while the supernatant liquid becomes yellow and deposits brilliant, brownish yellow, lamellated crystals. These, when exposed to the air on bibulous paper, become opaque and green, but retain their brilliancy. If again put into water they turn yellow, and yield a yellowish solution, together with a greenish blue residue.—2. If a cold boiled solution of carbonate of potash is used, the precipitate is sometimes obtained in the form of a dense yellow powder, sometimes in the form of bluish green flakes, which appear however to have the same constitution as the powder, inasmuch as, on dissolving the former in a fresh quantity of water, the flocculent precipitate is found to increase on standing.—If the yellow or brownish red solution is exposed to the air, it turns green, and at the same time a green substance separates, which is immediately precipitated on the addition of alcohol. When the liquid is kept in close vessels, it evolves carbonic acid, becomes turbid, and deposits the greenish, flocculent precipitate mentioned above: this likewise disengages carbonic acid and hydrogen gas, turns brown, and appears to be transformed into Peligot's hydrated chromoso-chromic oxide. The precipitate obtained from the cold potash solution does not change on boiling, excepting that it gives off carbonic acid, and afterwards dissolves in acids without effervescence. Bicarbonate of potash behaves like the simple salt, but evolves a larger quantity of carbonic acid, and retains more of the chromous carbonate in solution. (Moberg.) ¶

Carbonate of Chromic Oxide.—Prepared by precipitating a salt of chromic oxide with a moderate excess of carbonate of ammonia, potash, or soda. Light pale greenish blue powder. According to Meissner, it contains 77·30 per cent. of oxide, 15·54 of acid, and 7·16 of water. The carbonic acid is evolved at a temperature of 62°. (Meissner.) The salt is insoluble in water, but when recently precipitated, dissolves in an aqueous solution of carbonate of potash. ¶ According to Lefort, it consists of $Cr^2O^3, CO^2 + 4HO$, and loses 3 atoms of water between 75° and 150°; but the last atom of water and the carbonic acid are not evolved till the temperature exceeds 300°. (*Compt. rend.* 27, 269.) ¶

Chromium and Boron.

¶ Borate of Chromous Oxide.—Obtained by precipitating the protochloride with borax. Pale blue precipitate soluble in free acids, but insoluble in excess of the reagent. (Moberg.) ¶

Borate of Chromic Oxide.—*a*. Borate of ammonia precipitates from a solution of sesquichloride of chromium, even when largely diluted, a pale green powder, insoluble in water. (Hayes.) Borax produces a blue precipitate soluble in excess of the reagent. (Berlin.)—*b*. Sexborate of potash gives a green precipitate with chromic salts. (Laurent.)

Chromium and Phosphorus.

A. Diphosphide of Chromium.—1. Formed when phosphuretted hydrogen gas is passed over heated sesquichloride of chromium.

$$Cr^2Cl^3 + PH^3 = Cr^2P + 3HCl.$$

The resulting phosphide of chromium retains the crystalline scaly form of the chloride of chromium used. It is black; gives a phosphorescent flame before the blowpipe; does not dissolve in hydrochloric acid, and, to a very small extent and only after long boiling, in nitric or nitrohydrochloric acid. (H. Rose, *Pogg.* 24, 333.)—2. Phosphate of chromic oxide is pressed down into a charcoal crucible and heated in a blast-furnace.—The product is a slightly coherent, light grey, somewhat brilliant mass, which conducts electricity, undergoes but slight change in an open fire, and is oxidized with difficulty in the outer blowpipe flame. It is decomposed by hydrate of potash at a red heat only, a gas being evolved which burns with a yellow flame, and without any odour of phosphorus; after a long interval, the yellow colour of chromate of potash appears. It scarcely imparts any colour to boiling aqua-regia, even after digestion with it for many hours; it is insoluble in all other acids, even the hydrofluoric. (Berzelius.)

	Calculation.		H. Rose.
2Cr	56·0	64·07	64·5
P	31·4	35·93	35·5
Cr^2P	87·4	100·00	100·0

B. PHOSPHITE OF CHROMIC OXIDE.—An aqueous solution of sesquichloride of chromium is precipitated by terchloride of phosphorus dissolved in water and neutralized with ammonia. The phosphite of chromic oxide remains partially dissolved, imparting a green colour to the liquid; it likewise redissolves in the wash-water; but on heating these solutions, it is perfectly precipitated, leaving the supernatant liquid colourless. Loose, green powder, which, when ignited in a retort, evolves hydrogen gas free from phosphorus and without any appearance of light. (H. Rose, *Pogg.* 9, 40.)

¶ C. PHOSPHATE OF CHROMOUS OXIDE.—Phosphate of soda produces in a solution of the protochloride an abundant blue precipitate, which is readily dissolved by acids, and rapidly turns green on exposure to the air. (Moberg.) ¶

D. PHOSPHATE OF CHROMIC OXIDE.—*a. Neutral Phosphate.* On mixing sesquichloride of chromium with phosphate of potash, a green precipitate is obtained, which appears bluish black after ignition, but yields a greenish brown powder.

b. Acid Phosphate.—Hydrated sesquioxide of chromium yields with aqueous phosphoric acid an emerald-green, uncrystallizable solution. (Vauquelin.)

¶ E. PYROPHOSPHATE OF CHROMIC OXIDE.—Formed by precipitating a solution of crystallized chrome-alum with pyrophosphate of soda. At ordinary temperatures, a dirty red precipitate appears; but with a boiling solution, a pale green precipitate is obtained. This salt is soluble in solution of pyrophosphate of soda; in strong mineral acids; in water acidulated with sulphuric acid, from which it is again precipitated in an amorphous state on boiling; and in solution of potash. At 100°, it assumes a deeper green colour, but after ignition appears paler. The hydrate contains 7 atoms of water. (Schwarzenberg, *Ann. Pharm.* 65, 2.)

	Calculation.		Schwarzenberg.
$2Cr^2O^3$	160·0	42·76	41·46
$3PO^5$	214·2	57·24	58·54
$2Cr^2O^3, 3PO^5$	374·2	100·00	100·00

F. METAPHOSPHATE OF CHROMIC OXIDE.—Prepared by Maddrell (*Mem. of Chem. Soc.* 3, 273) by dissolving chromic oxide in excess of dilute phosphoric acid, and heating the dry mass to 316°. Beautiful green, anhydrous salt, insoluble in water and concentrated acids. ¶

	Calculation.		Maddrell.
Cr^2O^3	80·0	27·269	27·164
$3PO^5$	214·2	72·731	72·836
$Cr^2O^3, 3PO^5$	294·2	100·000	100·000

CHROMIUM AND SULPHUR.

A. SULPHIDE OF CHROMIUM. ¶—1. *Protosulphide.*—By igniting the red sulphate of chromic oxide in a current of hydrogen gas, Traube obtained a highly pyrophoric mixture of *protosulphide of chromium* and chromic oxide = $CrS+Cr^2O^3$. He does not, however, appear to have separated the protosulphide, or to have studied many of its properties.—2. Protochloride of chromium gives a black precipitate with sulphide of ammonium. (Moberg.) ¶

b. Sesquisulphide.—1. Formed by passing the vapour of bisulphide of carbon over chromic oxide heated to whiteness in a porcelain tube. (H. Rose.)—2. By passing hydrosulphuric acid gas over strongly ignited sesquichloride of chromium [or the red sulphate of chromic oxide, *Traube*], (Liebig, Harten, *Ann. Pharm.* 37, 349.)

$$Cr^2Cl^3 + 3HS = Cr^2S^3 + 3HCl.$$

3. By heating an intimate mixture of hydrated chromic oxide and sulphur in a close vessel. (Berzelius.)—4. By fusing chromic oxide with pentasulphide of potassium at a very high temperature, and dissolving out the sulphide of potassium by water. (Berzelius.) Chromic oxide may also be fused with sulphur and carbonate of potash. (Fellenberg, *Pogg.* 50, 77.)—5. By heating sesquichloride of chromium and 5 parts of sulphur to redness in a retort. (Lassaigne.) In this case, according to Berzelius, the decomposition is not complete.

Sesquisulphide of chromium, as prepared by the second method, is black, and sometimes of a crystalline shining texture (Liebig); sometimes pulverulent. (Harten.) As prepared by the third method, it is dark grey, and yields a black powder, which, when pressed, becomes coherent, and assumes the metallic lustre. (Berzelius.) The fourth method yields green shining scales, like pounded graphite (Berzelius), soft and unctuous to the touch. (Fellenberg.) By the fifth method, an iron-black, unctuous, very light mass is obtained, which readily imparts a stain. (Lassaigne.)

	Calculation.		Fellenberg, 4.	Harten, 2.	Lassaigne, 5
2Cr	56	53·84	53·5	51·02	90·46
3S	48	46·16	46·5	43·70	9·54
Cr^2S^3	104	100·00	100·0	94·72	100·00

Sesquisulphide of chromium, when heated to redness in the air, burns like a pyrophorus, yielding sulphurous acid gas and a residue of sesquioxide. (Lassaigne.) At a red heat, it decomposes aqueous vapour, forming hydrosulphuric acid and a small quantity of green sesquioxide. (Regnault, *Ann. Chim. Phys.* 62, 381.) It is partially decomposed by chlorine at ordinary temperatures [illegible] fectly with the aid of heat, sesquichloride of chromium being sublimed. (Berzelius, Fellenberg, Harten.) Chlorine scarcely acts on it, even at high temperatures. (H. Rose, *Pogg.* 42, 541.) By aqua-regia it is converted into sesquichloride of chromium and sulphuric acid (Lassaigne); by nitric acid, according to Berzelius, it is decomposed with difficulty; according to Lassaigne, no decomposition takes place, even when the acid is boiled with it. When ignited with nitre, it yields sulphate and chromate of potash. (Lassaigne.) It is not dissolved by potash, or by hydrosulphate of potash. (Berzelius.)

c. Tersulphide of Chromium? [Vid. *Tersulphide of Chromium with Hydrosulphate of Ammonia*, and *Tersulphide of Chromium with Sulphide of Potassium.*]

¶ B. Sulphite of Chromous Oxide.—Obtained from the protochloride by double decomposition. Brick-red precipitate, which, when washed out of contact of air, becomes chestnut-brown after some days, and gradually assumes a bluish green colour, proceeding from the surface inwards. In the air, these changes take place very rapidly, in consequence of the conversion of the salt into basic sulphite of chromic oxide. (Moberg.) ¶

C. Sulphite of Chromic Oxide.—An aqueous solution of sulphurous acid readily dissolves the hydrated sesquioxide. (Vauquelin.) The green solution deposits, on boiling, [or on the addition of alcohol,] the whole of the oxide, as a green, granular, basic salt [a whitish green powder, which has a sulphurous taste, and gives off sulphurous acid when heated: *Muspratt*]. Neither ammonia nor carbonate of potash or soda precipitates a cold solution of the salt; but from a hot solution, these reagents throw down the whole of the chromium: the cold solution, mixed with ammonia, has a pale wine-red colour. The alkaline sulphites do not precipitate the chromic salts, even after long boiling. (Berthier, *Ann. Chim. Phys.* 50, 370; *N. Ann. Chim. Phys.* 7, 77.) According to Berlin, sulphite of potash precipitates the hydrochlorate of chromic oxide.

D. Hyposulphate of Chromic Oxide.—Cr^2O^3, S^2O^5.—Small violet-coloured octohedrons, soluble in water. (Berlin.)

¶ E. Sulphate of Chromous Oxide.—Peligot (*N. Ann. Chim. Phys.* 12, 548) states that on treating the metallic powder reduced from the violet sesquichloride of chromium by potassium, with dilute sulphuric acid, hydrogen gas is disengaged, and a solution obtained which exhibits the characters of a chromous salt. ¶

F. Sulphate of Chromic Oxide.—*a. Two-thirds Sulphate.*—Precipitated on mixing a concentrated solution of *b* with water, and also on heating the resulting clear supernatant liquid. In the hydrated state, it forms a light-green, very hygroscopic powder, which, when heated, first loses the whole of its water, without fusing, and then, at a low red heat, gives off all its sulphuric acid, leaving chromic oxide of a rather dark green colour. It gives up the whole of its sulphuric acid when digested for some time with caustic potash or carbonate of potash. It is insoluble in water, but dissolves in acids, though with greater difficulty in proportion as it has been more quickly dried. (Schrötter, *Pogg.* 53, 513.) Vauquelin likewise obtained an insoluble basic salt by strongly heating the salt *b*. From a solution of potash chrome-alum, caustic ammonia or carbonate of ammonia precipitates a greyish-red basic salt, which appears pale blue after drying, and dissolves slowly but perfectly in acids, forming a violet solution. (Berzelius.)

	Anhydrous.			*Hydrated.*		Schrötter.
$3Cr^2O^3$	240	75	$3Cr^2O^3$	240	53·81	53·02
$2SO^3$	80	25	$2SO^3$	80	17·94	18·29
			$14HO$	126	28·25	28·21
$3Cr^2O^3, 2SO^3$	320	100	$+14Aq.$	446	100·00	99·52

b. Bisulphate.—Dilute sulphuric acid is saturated with hydrated chromic oxide by long boiling and concentration. The dark green solution, which is acid to test-paper, leaves on drying a green amorphous mass, from which the whole of the sulphuric acid is expelled by ignition. The solution exhibits a dark ruby colour by transmitted sun-light or candle-light. (Schrötter.) If the above solution, which appears green by day and red by candle-light, be introduced into a hollow prism whose refracting angle is between 5° and 10°, and the prism be then placed between the eye and a candle, two images of the candle appear, one red and the other green; the rest of the spectrum is absorbed; so that a kind of double refraction is produced. If the solution is placed in a bottle, and looked through, the two images overlap each other, the green predominating by daylight, the red by candle-light. (Talbot, *N. Br. Arch.* 5, 141.)

A concentrated solution of bisulphate of chromic oxide is rendered turbid by the addition of water, depositing a larger quantity of the salt *a*, and becoming paler coloured in proportion to the amount of water added; on evaporation, however, the precipitate is redissolved. The dilute solution filtered from the precipitate, deposits when heated a fresh quantity of the salt *a*, which again disappears on boiling. A solution of specific gravity 1·219 and above, deposits nothing when heated; a solution of 1·166 becomes turbid at 57°; of 1·037 to 1·031, at 64°; of 1·002, at 45°; and of 1·001, at 55°; a still more dilute solution remains clear even at a boiling heat. (Schrötter.)

	Anhydrous.		Schrötter.
Cr^2O^3	80	50	50·44
$2SO^3$	80	50	49·56
$Cr^2O^3, 2SO^3$	160	100	100·00

c. Tersulphate.—*α. Insoluble.*—If a green pasty mixture of the salt *b* with oil of vitriol, is heated till the sulphuric acid begins to volatilise, it immediately assumes a pale peach-blossom colour. With a large quantity of oil of vitriol, a green limpid mixture is obtained, which, when heated, becomes colourless, and deposits a peach-blossom coloured powder. The red salt, which, after cooling, appears pale reddish grey, is purified with water and then dried. It exhibits a very light red tint in diffused daylight; very pale green in the direct rays of the sun; and verdigris-green by candle-light. Every time it is heated, it assumes a beautiful peach-blossom colour. When long ignited over the flame of a spirit-lamp, it loses the whole of its sulphuric acid. Ignited in a current of hydrogen gas, it yields water, hydrosulphuric acid, sulphur, and sesquioxide of chromium. It is readily decomposed by fused or boiling caustic potash or soda, and slowly and imperfectly by a boiling solution of carbonate of potash. It remains unchanged in ammonia, and is insoluble in water, sulphuric, hydrochloric, nitric, or nitro-hydrochloric acid. (Schrötter.)

¶ Traube states that this salt is really an acid salt of chromic oxide, and that it is probably formed when any salt of chromic oxide is heated with strong sulphuric acid, he himself having prepared it from the hydrated oxide, from chrome-alum, and from chromate of potash (the bichromate yields a compound of the same salt with sulphate of potash, the proportions varying according to the temperature). According to Traube, also, it is grey by daylight, and green by candle-light, and forms sometimes a granular, sometimes a soft powder, so fine indeed that it passes through the filter. In the finely divided state it likewise remains suspended in water for a considerable time, but may be rapidly thrown down by the addition of various salts, as sal-ammoniac, &c. It is insoluble in cold water, but by long boiling or by long standing in contact with water, it is partially converted into a soluble modification. It is likewise insoluble in ammonia and the strong mineral acids. It is decomposed by ignition in a current of hydrogen gas, the volatile products being water, sulphur, sulphurous acid, and lastly, hydrosulphuric acid—the residue, a black, pyrophoric mixture of protosulphide of chromium and chromic oxide. A current of hydrosulphuric-acid gas at a high temperature converts it into black sesquisulphide of chromium, with disengagement of sulphur, sulphurous acid, and water. Its formula is $2(Cr^2O^3,3SO^3) + HO,SO^3$. ¶

	Dried at 100°		Schrötter.
Cr^2O^3	80	40	40·08
$3SO^3$	120	60	59·40
$Cr^2O^3, 3SO^3$	200	100	99·48

	According to Traube.		
$2Cr^2O^3$	160	35·63	34·13
$7SO^3$	280	62·36	62·90
HO	9	2·01	3·18
KO			0·12
$2(Cr^2O^3,3SO^3) + HO, SO^3$	449	100·00	100·33

β. *Soluble form.*—1. *Green, amorphous modification.* Eight parts of hydrated chromic oxide dried at 100°, are dissolved in 9 parts or rather more of warm oil of vitriol. The light of a candle transmitted through the green solution of this salt is ruby-coloured, and the solution does not yield crystals on evaporation or on the addition of alcohol. Evaporated at a temperature above 100°, it leaves a green, tenacious mass, containing either 5 or 6 atoms of intimately combined water, which is expelled when the substance is heated to the boiling point of linseed oil; at that temperature, the salt is converted into the insoluble peach-blossom coloured salt α. (Schrötter.)

2. *Blue, crystalline modification.*—1. A solution of 8 parts of hydrated chromic oxide in 9 parts of cold sulphuric acid left to itself in a covered basin, solidifies in the course of a few weeks to a greenish blue crystalline mass. This forms with water a dark blue solution, which exhibits a beautiful ruby-colour by transmitted candle-light. Alcohol precipitates from it a pale violet-coloured, crystalline powder, and decolorizes the liquid. It is only when there is an excess of acid (which is better) or a deficiency, that the solution remains green. To obtain good crystals, the crystalline powder is collected on a filter—dissolved in a moderate quantity of water—dilute alcohol added nearly to the point at which a precipitate appears—and the solution left to evaporate spontaneously in a vessel covered with a bladder.

¶ 2. Traube prepares this compound by dissolving 1 part of purified chromic acid in 3 parts of water, and suffering alcohol to drop into the mixture from a funnel stopped up with paper. As soon as the reduction of the chromic acid is complete, absolute alcohol is added—whereby the blue compound is immediately precipitated—and the precipitate washed with alcohol. Should the temperature rise in the first instance from incautious addition of alcohol, and the green modification be thereby produced, the solution must be boiled with nitric acid—which (according to Löwel) rapidly converts the green into the violet compound—and then precipitated by alcohol.—3. It may also be obtained by dissolving 1 part of chromic acid in 1½ parts of strong sulphuric acid and 2¼ parts of water, and pouring the mixture into a wide basin in which a porcelain crucible containing ether is placed. The whole mass solidifies after some hours, forming small crystals of chromic sulphate. To complete the reduction, a few drops of alcohol are finally added. ¶

The salt crystallizes in regular octohedrons, of the colour of chrome-alum, and of specific gravity 1·696; soluble in 0·833 parts of water at 20°. At a temperature of 100°, the crystals lose 10 [or 9 ?] atoms of water, and pass into the green amorphous modification—and then, if heated above the boiling point of linseed-oil, into the red, insoluble modification α. An aqueous solution of the crystals becomes green at a temperature of 65° or 70°, from formation of the green, amorphous modification. ¶ By adding strong alcohol to this solution, a green syrup is precipitated, which, by shaking, or after some hours' standing, partly solidifies, yielding crystals of the blue salt. If, however, the violet solution be boiled for a long time, and then treated with strong alcohol, a green syrup is precipitated, which remains fluid even after several days. The blue salt may be boiled with alcohol (with a boiling point of 80°) without conversion into the green modification. (Traube.) ¶

If the blue solution of the salt, not very highly concentrated, be placed in a narrow glass tube, and a deep stratum of absolute alcohol carefully poured on the top of it, so as to prevent precipitation, the solution gradually assumes a green colour, proceeding from the top downwards, doubtless because the alcohol removes from the blue salt a portion of the water necessary to its constitution. (Schrötter.)

	Crystallized and dried at 30°			Schrötter.
Cr^2O^3	80	....	23·88	24·415
$3SO^3$	120	....	35·82	35·472
$15HO$	135	....	40·30	40·113
$Cr^2O^3, 3SO^3 + 15Aq.$	335	....	100·00	100·000

G. Brown Sulphate of Chromic Oxide.—Brown oxide of chromium yields, with sulphuric acid, a dark brown solution, which becomes green when exposed to light. (Berzelius.) If the solution is saturated with oxide, it leaves on evaporation, a yellowish brown mass, which, after exposure to light for a few hours, is converted into the ordinary green sulphate. If the sulphuric acid is in excess, there remains a red, dingy-looking mass, which soon becomes green, and when heated till the sulphuric acid volatilizes, leaves an insoluble, dirty-white basic salt. (Brandenburg.)

H. Sulphate of Chromic Acid?—By mixing aqueous chromic acid with sulphuric acid, or by decomposing chromate of baryta or chromate of lead with excess of boiling sulphuric acid, Gay-Lussac (*Ann. Chim. Phys.* 16, 102; also *Schw.* 32, 447) obtained dark red, deliquescent prisms, which, from his analysis, appear to consist of sulphate of chromic acid = CrO^3, SO^3.—The experiments of Fritzsche, however (p. 117, 4), confirmed by Hagen and Plantamour, have proved that these crystals are nothing more than chromic acid, with from 8 to 10 per cent. of mechanically adhering sulphuric acid, which, by drying the crystals on a brick or between folds of blotting paper, may be reduced to 1·8 per cent. ¶ Bolley (*Ann. Pharm.* 56, 113) finds that chromic acid is less soluble in bihydrated sulphuric acid than in the same acid of any other strength. When crystallized chromic acid is thrown, by small portions at a time, into strong sulphuric acid, till no more is dissolved on agitation, a dark brown, oleaginous solution is formed, which afterwards becomes deep yellow and pasty. After standing for a day or two, this liquid acquires a pale brown tint with a tinge of green, and becomes granular. When rapidly dried on burnt clay, it yielded the following results:

	Calculation.		Bolley.
CrO^3	52	51·48	47·4
SO^3	40	39·61	42·8
HO	9	8·91	9·7
$CrO^3, SO^3 + HO$	101	100·00	99·9

The excess of sulphuric acid probably arises from a portion of that substance adhering to the crystals. ¶

I. Sulphocarbonate of Chromium.—Sulphocarbonate of lime gives with salts of chromic oxide a greyish green precipitate, resembling the hydrated sesquioxide. By distillation it yields bisulphide of carbon, and a brown residue of sesquisulphide of chromium, which burns vividly in the open fire, and forms chromic oxide. (Berzelius.)

¶ Selenium and Chromium.

Selenite of Chromium.—*a. Neutral Selenite.*—$Cr^2O^3,3SeO^2$.—Prepared by decomposing chloride of chromium by selenite of ammonia. Soft, green, amorphous powder.

	Calculation.		Muspratt.
Cr^2O^3	80	32·26	32·60
$3SeO^2$	168	67·74	
$Cr^2O^3, 3SeO^2$	248	100·00	

b. Acid Selenite.—Selenite of chromium dissolves in selenious acid, yielding a green varnish on evaporation. (Muspratt, *Qu. J. of Chem. Soc.* 5, 62.) ¶

Chromium and Iodine.

¶ Protochloride of chromium is not precipitated by iodide of potassium; but the mixture acquires a reddish brown colour. (Moberg.) ¶

A. Iodide of Chromium ?—According to H. Rose (*Pogg.* 27, 575), a mixture of bichromate of potash and iodide of potassium with oil of vitriol yields nothing but iodine when distilled. Giraud, on the contrary, thought that he obtained teriodide of chromium by the following process: when a mixture of 33·5 parts of monochromate of potash and 165·5 parts of iodide of potassium is mixed in a retort with 70 parts of oil of vitriol, the mixture becomes strongly heated, gives off (besides sulphuric acid and free iodine) deep red vapours; and after being sufficiently heated, leaves a residue of sulphate of potash and sulphate of chromic oxide in the retort. The red vapours condense into a deep red oil, which is heavier than water, and boils at about 149°, giving off a dense red vapour. The oil imparts a deep brownish red permanent stain to the skin, and destroys the cuticle; corrodes and blackens paper and wood; absorbs water from the air; and yields with water a solution of chromic and hydriodic acids. (Giraud, *Phil. Mag. J.* 12, 322.)—No analysis of this substance was undertaken.

A solution of bichromate of potash gives with excess of concentrated hydriodic acid, a dense, black precipitate, while a large quantity of free iodine is separated; the precipitate when dry resembles gum-kino, and dissolves in water, forming a green solution. (Inglis.)

B. Iodate of Chromic Oxide.—Iodate of soda produces in a solution of sesquichloride of chromium, a dark blue, pulverulent precipitate, which assumes a lighter colour when dry. (Berlin.)

Chromium and Bromine.

¶ Protochloride of chromium forms a dark green mixture with bromide of potassium. (Moberg.) ¶

A. Sesquibromide of Chromium and Hydrobromate of Chromic Oxide.—1. Metallic chromium heated with bromine in a glass tube, the top of which is closed with the finger, does not absorb the bromine till it is red-hot, at which time the bromine is of course in the state of vapour; combination then takes place, attended with emission of light and heat. The product is a greyish green, deliquescent mass, having a sweet and rough taste. (Berthemot, *Ann. Chim. Phys.* 44, 383; also *J. Pharm.* 16, 650.)

The green solution of sesquibromide of chromium in water turns brown on evaporation, and crystallizes with difficulty. When it is further evaporated, the residue evolves hydrobromic acid, and at a dull red heat, vapours of bromine are given off; exposure to a white heat converts it wholly into sesquioxide of chromium. A similar solution is obtained by saturating aqueous hydrobromic acid with hydrated chromic acid, in which case bromine is set free. (Berthemot.)—By agitating chromate of lead with aqueous hydrobromic acid and boiling the filtrate, a dark green solution is obtained, which does not yield crystals on evaporation; but when evaporated to dryness and ignited, leaves a yellowish red powder. (Löwig.)—Bromine-water partially converts the green hydrate of chromic oxide into the brown modification; the filtrate after evaporation deposits green crystals of hydrobromate of chromic oxide. (Balard.)

When bichromate of potash is heated with bromide of potassium and oil of vitriol, bromine alone distils over, without a trace of chromium. (H. Rose, *Pogg.* 27, 575.)

B. Bromate of Chromic Oxide.—Sulphate of chromic oxide is precipitated by bromate of baryta and the solution filtered.—The green filtrate evaporated over a water-bath soon gives off bromine, and assumes a yellowish red colour, leaving a dark red, crystalline, deliquescent mass, which *consists almost entirely of chromic acid.* (Rammelsberg, *Pogg.* 55, 87.)

Chromium and Chlorine.

¶ A. Protochloride of Chromium.—*Formation and Preparation.*—1. By passing dry chlorine gas over a red-hot mixture of chromic oxide and charcoal—sesquichloride (*q. v.*) being formed at the same time. (Peligot.)—2. By passing hydrogen gas over perfectly anhydrous sesquichloride of chromium very gently heated, as long as hydrochloric acid gas continues to be given off ($Cr^2Cl^3 + H = HCl + 2CrCl$). The hydrogen must be freed from all traces of oxygen by passing it through a solution of protochloride of tin in caustic potash, then through tubes containing sulphuric acid and chloride of calcium, and lastly over ignited metallic copper.

The protochloride obtained by the first method is in fine white crystals, usually mixed, however, with charcoal and chromic oxide. The second method yields a white velvety substance, which retains the form of the sesquichloride from which it has been prepared.

	Calculation.		Peligot.		
			1.	2.	3.
Cr	28·00	44·15*	39·4	42·7	42·0
Cl	35·41	55·85	58·4	56·7	57·0
$CrCl$	63·41	100·00	97·8	99·4	99·0

Protochloride of chromium dissolves in water, with evolution of heat, and forms a blue solution, which, when exposed to the air, rapidly turns green, from absorption of oxygen. It likewise turns green when exposed to the action of chlorine. If kept out of contact of air, it gives with caustic potash a brown precipitate of hydrated protoxide, accompanied by disengagement of hydrogen. With ammonia it gives a greenish white precipitate, without evolution of hydrogen. With ammonia and sal-ammoniac it forms a blue liquid, which turns red on exposure to the air. Monosulphide of potassium gives a black precipitate containing sulphur, and insoluble in excess.—Ferrocyanide of potassium gives a yellowish green precipitate.—The solution of protochloride of chromium is one of the most powerful deoxidizing agents known. With a solution of monochromate of potash, it gives a brown precipitate, probably consisting of chromoso-chromic oxide: if the protochloride be added in excess, the precipitate disappears, and the liquid becomes green. It precipitates calomel from a solution of corrosive sublimate. With a salt of protoxide of copper, it gives a white precipitate of dichloride of copper; but if it be added in excess, a red precipitate of dioxide of copper is produced. It instantly converts tungstic acid into blue oxide of tungsten, and precipitates metallic gold from a solution of the chloride, with evolution of hydrogen.

Subchloride of Chromium.—Obtained, according to Moberg, by treating a solution of the protochloride with ammonia. The precipitate cannot be obtained free from ammonia; hence its composition has not been determined. The supernatant liquid retains its blue colour in close vessels; but when exposed to the air, it is converted into ammonio-chloride of chromium. The precipitate turns green in the air—dissolves with tolerable facility in hydrochloric acid, the act of solution, if performed in a close vessel, being attended with evolution of hydrogen. (Moberg, *Pharm. Centralb.* 1848, 787.) ¶

B. SESQUICHLORIDE OF CHROMIUM.—1. An aqueous solution of ter-hydrochlorate of chromic oxide is evaporated to dryness, and the residue heated to expel the last traces of water. (Vauquelin.) The solid residue obtained at a gentle heat forms a bulky rose-coloured powder, which, when strongly heated in a retort, evolves chlorine, diminishes in volume, and is converted into yellow micaceous scales.

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* According to Peligot, the atomic weight of chromium is 26·241, which gives for the protochloride, 42·6 Cr + 57·4 Cl, agreeing very nearly with the results of analysis.

(Vauquelin.)—Evaporated at 100°, the solution leaves a dark green deliquescent mass, which does not part with the whole of its water even at 160°, but remains unaltered. At a still higher temperature, it loses water, swells up strongly, and assumes a peach-blossom colour; but the last portions of water can only be expelled by exposure to a high temperature, and their evolution is attended with partial decomposition of the compound. Even when the residue is heated in an oil bath to 250°, and a current of dry air passed over it, traces of water still remain; at the same time, chlorine is evolved, and a portion of the sesquichloride of chromium is converted by the oxygen of the air into chromic oxide, which imparts a green colour to the mixture. (H. Rose.)—2. Berzelius introduces the residue obtained by evaporating hydrochlorate of chromic oxide into a retort and heats it till it sublimes, whereby a small quantity only of hydrochloric acid is set free. Only the smaller portion sublimes as insoluble chloride of chromium, the larger quantity remaining in the retort in the soluble form. (Berzelius.)—Gaulthier de Claubry (*Ann. Ch. Ph.* 45, 110; also *Schw.* 62, 217) by evaporating a solution of hydrochlorate of chromic oxide to dryness, putting the dry residue into a porcelain retort, and heating it to whiteness in a blast-furnace till the retort began to soften, obtained a large quantity of sesquichloride of chromium sublimed in peach-blossom coloured needles; a considerable portion, however, remained unvolatilized.—3. The residue obtained as above by evaporating a solution of hydrochlorate of chromic oxide, is ignited in a current of chlorine gas. If the chlorine contains atmospheric air, sesquioxide of chromium is also produced, with incandescence. (H. Rose.)—4. Sulphide of chromium is heated in a current of dry chlorine gas. (Berzelius; Fellenberg, *Pogg.* 50, 79.)—5. Dry chlorine gas is passed over an ignited mixture of sesquioxide of chromium and charcoal. (Wöhler, *Pogg.* 11,148.) The heat of an argand spirit-lamp is sufficient for the purpose. (Wöhler.)—No higher chloride is formed even with a large excess [of sesquioxide?] and at very high temperatures. (H. Rose.) The chloride of chromium being but slightly volatile, sublimes as it forms and collects in that part of the tube which still contains charcoal. The mixture of chloride and charcoal is therefore introduced into a fresh glass tube, so as only to cover the bottom, and strongly ignited in a current of chlorine gas. The pure chloride of chromium sublimes into the upper portion of the tube. (H. Rose.)

Sesquichloride of chromium has a soluble and an insoluble modification; the former is obtained by the first method, the latter by the second, third, and fourth (H. Rose); the fourth method yields a mixture of a small quantity of soluble with a large quantity of insoluble chloride. (Fellenberg.) Both modifications have the form of brilliant, peach-blossom coloured, micaceous laminæ, which, when thin, transmit light of the same colour. They leave a mark on the skin like talc. (H. Rose.) They volatilize at a bright red heat. ¶ According to Peligot, the sesquichloride by itself is perfectly insoluble in water, but when in contact with the protochloride, it dissolves with ease, heat being evolved and a green solution formed: this solution exhibits all the characters of chromic salts. A very small quantity, less than $\frac{1}{10,000}$, of the protochloride is sufficient to render the sesquichloride soluble: the protochloride appears to act merely by contact. ¶

	Calculation.		Berzelius.	Fellenberg.
2Cr	56·0	34·52	36·14	35·2
3Cl	106·2	65·48	63·86	64·8
Cr^2Cl^3	162·2	100·00	100·00	100·0

Sesquichloride of chromium ignited in the air evolves chlorine, and is first converted into oxychloride of chromium, and then into sesquioxide. In the case of the soluble modification, the change is attended with emission of light and heat. The insoluble variety, which does not glow, leaves 47·54 per cent. of sesquioxide. (H. Rose.) The red sublimed chloride of chromium heated in a stream of hydrogen gas as strongly as the glass tube will bear, is converted, with loss of 24·57 per cent. of chlorine, into a white substance, which is probably CrCl. (p. 130) The latter substance deliquesces in the air and becomes green; when moistened with water it becomes heated, emits a smell of hydrogen gas, turns green, and dissolves in water, with the exception of 7·5 per cent. of a green powder, which, if treated with ammonia, assumes a deep blue colour, and partially dissolves in it, forming a beautiful red solution. (Moberg, *J. pr. Chem.* 29, 279.)—By ignition in phosphuretted hydrogen gas, the sesquichloride is converted into phosphide of chromium. (H. Rose.) When heated with sulphur (Lassaigne) or in a stream of hydrosulphuric acid gas (Liebig), it yields sulphide of chromium. Ignited in ammoniacal gas it yields nitride of chromium. (Schrötter.) When fused with carbonate of soda and sal-ammoniac, it yields, not metallic chromium, but chromic oxide in crystalline spangles. (Wöhler.) The soluble chloride of chromium is readily decomposed by alkalis. The insoluble variety is acted on with difficulty by a boiling solution of caustic potash, and with still greater difficulty by a boiling solution of carbonate of potash or soda; solution of ammonia has no effect upon it. (H. Rose.) According to Fellenberg, boiling caustic potash or soda and their carbonates easily remove the hydrated oxide. The soluble chloride is immediately decomposed by warm sulphuric acid, yielding hydrochloric acid and solid sulphate of chromic oxide. The insoluble chloride is not decomposed by boiling sulphuric acid either concentrated or dilute, nor even when heated with anhydrous sulphuric acid, which volatilizes without acting upon it. (H. Rose.) Boiling hydrochloric, nitric, and nitro-hydrochloric acid, likewise have no action on this substance. (Fellenberg.)—¶ According to Jacquelain—who regards the violet chloride before washing as a compound of protochloride and sesquichloride of chromium—it is soluble in 2,000 parts of water at 90°, in 1000 parts at 100°; and in 68 parts at 136° under pressure. Moreover, it is slowly decomposed by sulphuric acid at ordinary temperatures, and more rapidly with the aid of heat, hydrochloric acid being evolved, and a green solution obtained. Sulphurous acid likewise decomposes it in close vessels, forming a green solution. ¶

Hydrated Sesquichloride of Chromium, or *Terhydrochlorate of Chromic Oxide.*—1. Formed by dissolving the sesquichloride of chromium in water. The soluble modification, even after being heated to 250°, deliquesces rapidly in the air, and yields a dark green solution. The insoluble chloride diffuses itself in water in fine scales, but even after long contact, a mere trace only is dissolved, producing a greenish colour in the liquid. (H. Rose.)—2. By dissolving the hydrated sesquioxide in aqueous hydrochloric acid.—3. By boiling chromic acid with hydrochloric acid. 4. By boiling red chromate of lead in hydrochloric acid, evaporating, and dissolving out the chloride of chromium by means of alcohol; or by boiling the mineral with hydrochloric acid and alcohol, and filtering the liquid. The solution appears dark green by reflected and red by transmitted light.—¶ 5. According to Peligot, this solution, when evaporated in vacuo, leaves an amorphous mass, which dissolves in water with disengagement of heat, and consists of $Cr^2Cl^3, 6HO$. When a solution of the insoluble violet chloride in water containing protochloride is slowly evaporated in vacuo, green (needle-formed, *Moberg*) crystals are obtained, which are very soluble in water, and consist of $Cr^2Cl^3 + 12HO$. ¶

On looking through a stratum of the above solution a line in thickness, the flame of a candle appears red; the sun and objects illuminated by it, even green leaves, appear rose-coloured; the clouds not directly illuminated by the sun, white; and the sky itself, greyish-blue. (Gmelin.) The thinner the stratum of liquid, the more highly must it be concentrated, in order to transmit candle-light red; if the solution be too dilute or the stratum too thin, the light appears green; indeed the colour varies with the method by which the solution is prepared. For instance, the solution obtained by boiling chromate of lead with hydrochloric acid and alcohol appears red at a much greater degree of dilution and in a much thinner stratum, than the saturated solution of hydrated chromic oxide in hydrochloric acid; next to the latter stands the solution obtained by treating chromate of lead with hydrochloric acid and alcohol in the cold. A solution diluted till its density is reduced to 1·010, and kept for a long time at a temperature of 70°, acquires the property of appearing red by transmitted candle light, even when in very thin strata: if, however, it is evaporated or boiled for some time, it appears green by candle-light. (Moberg.)

The solution of sesquichloride of chromium has a sweet and afterwards rough taste. If slowly evaporated and afterwards heated to 100°, it leaves a dark green hydrated mass, which, according to Liebig, swells up strongly at a temperature of 200°....300°, and is converted into red soluble chloride of chromium.

C. Oxychloride of Chromium.—By boiling hydrochloric acid with an excess of hydrated chromic oxide, nothing but a solution of Cr^2Cl^3 is obtained.—*a.* $2Cr^2Cl^3, Cr^2O^3$.—1. A solution of sesquichloride of chromium evaporated and dried at 120°, swells up and crumbles on stirring, to a reddish-grey powder which deliquesces in the air.—2. If the substance be dried at 150°, with constant stirring, a greyish-red powder is obtained, which, when treated with cold water, leaves a rose-coloured residue. This latter compound dissolves in warm water; its analysis is given under (2) below.—3. If the solution is evaporated over oil of vitriol, the *hydratea compound* remains in the form of a dark red mass: analysis 3. (Moberg.) ¶ A solution of this compound gives with iodide of potassium a yellow, and with sulphite of potash, a blue greyish-green precipitate; with other salts it gives similar reactions to the neutral chloride. (Moberg.) ¶

	Calculation.		Moberg. (1)	Moberg. (2)
$2Cr^2Cl^3$	324·4	80·22	81·11	81·52
Cr^2O^3	80·0	19·78	18·89	18·48
$2Cr^2Cl^3 + Cr^2O^3$	404·4	100·00	100·00	100·00

			Moberg. (3)
$2Cr^2Cl^3$	324·4	66·83	66·76
Cr^2O^3	80·0	16·48	15·93
9HO	81·0	16·69	17·31
+ 9Aq.	485·4	100·00	100·00

b. $Cr^2Cl^3, 2Cr^2O^3$. The greyish-red powder obtained at 150° (B, *a*, 2), when strongly heated becomes gradually darker without swelling up;

after being heated nearly to redness, it dissolves but partially in water; the insoluble portion appears greyish-red by daylight, and green by candle-light; its composition is given below. By long continued ignition in the air, it is completely converted into the sesquioxide. (Moberg, *J. pr. Chem.* 29, 178.)

	Calculation.		Moberg.
Cr^2Cl^3	162·2	50·31	50·53
$2Cr^2O^3$	160·0	49·69	49·47
$Cr^2Cl^3, 2Cr^2O^3$	322·2	100·00	100·00

By dissolving the brown hydrated oxide of chromium in hydrochloric acid, a red solution is obtained, which, by the agency of light, or by boiling with hydrochloric acid, or by evaporation, is converted into green hydrated sesquichloride of chromium with evolution of chlorine. (Berzelius, Brandenburg.)

D. CHLOROCHROMIC ACID.—*Chromate of Terchloride of Chromium.*—This compound was formerly regarded as terchloride of chromium, till H. Rose discovered the chromic acid present in it. It is formed by distilling a salt of chromic acid with common salt and oil of vitriol in excess. 1. Ten parts (3 atoms) of common salt are fused with 16·9 parts (3 atoms) of monochromate of potash; the resulting mass is broken up into large fragments and introduced into a capacious, long-necked, tubulated retort, and 30 parts (12 atoms) of fuming oil of vitriol poured upon it. The powerful heat evolved on mixing the ingredients is sufficient to drive nearly the whole of the new compound over into the receiver, which must be kept cool by moistened paper; that which passes over subsequently, on the application of heat [to be collected in a separate receiver], amounts to a small quantity only, and contains sulphuric acid. In the retort there remains a mixture of bisulphate of potash and soda, having a slight green tinge. (Wöhler, *Pogg.* 33, 343.)

$$3(KO, CrO^3) + 3NaCl + 12(HO, SO^3) = 3(KO, 2SO^3 + HO) + 3(NaO, 2SO^3 + 3HO) \\ + CrCl^3, 2CrO^3.$$

Three atoms of water are here assumed as existing in bisulphate of soda; which agrees with the determination of Brandes. (III., 104.) The fact that free chlorine is always disengaged in this process, and a portion of free chromic oxide found in the residue, proves that the decomposition partly takes place as follows:

$$3NaCl + 2(KO, CrO^3) + 13SO^3 = 3(NaO, 2SO^3) + 2(KO, 2SO^3) + Cr^2O^3, 3SO^3 + 3Cl.$$

The water which is present appears to give rise to this mode of decomposition. Walter (*Ann. Chim. Phys.* 66, 387; also *Pogg.* 45, 154), uses the same proportions, but introduces the oil of vitriol into the retort gradually, and through an S-tube, so that the mass may not boil over; and in order to condense the vapours perfectly, he cools the neck of the retort and receiver with great care, so that nothing but free chlorine may escape; and lastly, applies a gentle heat to the retort till yellow instead of red vapours appear. Bichromate of potash may also be used in place of the monochromate. (Wöhler, H. Rose.) Thomson uses 12 parts of bichromate of potash and 10 parts of common salt.

2. Dumas (*Ann. Chim. Phys.* 31, 435) distils common salt with chromate of lead and oil of vitriol, and condenses the vapours in a tube cooled to a very low temperature. The distillate contains an excess of

chlorine, which it has absorbed, and if the receiver is kept very cold, the quantity of that element is so great, that the liquid partially solidifies. (Dumas, H. Rose.) The compound is purified by partial distillation, whereupon the excess of chlorine is evolved and the sulphuric acid left behind in the residue. (Walter.)

Splendid blood-red liquid, which appears black by reflected light; at 21° its specific gravity is 1·71; and under a pressure of 0·76 metres, (= 29·92 in.), its boiling point is constant at 118°. (Walter.) Its vapour has the colour of hyponitric acid gas. [For the specific gravity of the vapour, see I., 280.]

	Calculation.	
$CrCl^3$	134·2	56·34
$2CrO^3$	104·0	43·66
$CrCl^3, 2CrO^3$	238·2	100·00

Or:			H. Rose.	Walter.
3Cr	84·0	35·27	35·53	35·18
3Cl	106·2	44·58	45·60	45·14
6O	48·0	20·15		
	238·2	100·00		

	Volume.	Sp. gr.
Vapour of chromium ?	1	1·9404
Chlorine gas	1	2·4543
Oxygen gas	1	1·1093
Vapour of chloro-chromic acid	1	5·5040

The compound may also be regarded as CrO^2Cl, or as chromic acid in which one atom of oxygen is replaced by one atom of chlorine; according to this view, Walter calls it *Chloro-oxychromic acid.*

The vapour passed through a red-hot tube is decomposed into crystallized chromic oxide (p. 111) and chlorine and oxygen gases. (Wöhler.)

$$2(CrO^2Cl) = Cr^2O^3 + O + 2Cl.$$

This compound explodes with phosphorus, the explosion being attended with emission of light. (Dumas, Walter.) A single drop of the liquid with a piece of phosphorus of the size of a pin's head, is sufficient to produce this effect. (Dumas.) The phosphorus must be moistened to produce the explosion; when dry it is without action, and ignited phosphorus is extinguished in the vapour of the compound. (Thomson.) Sulphur decomposes the compound with a hissing noise. (Dumas.) Flowers of sulphur moistened with it take fire after a few minutes, and burn with a red flame. (Thomson, *Phil. Mag. Ann.* 1, 452; also *Kastn. Arch.* 11, 217.) Sulphur separates a rose-coloured powder, (Kemp, *J. Pharm.* 20, 413), which, according to Gregory, has the same composition and properties as the insoluble sesquichloride of chromium. If sulphuretted hydrogen is passed into the compound, the tube containing it becomes red-hot; hydrochloric acid gas is evolved, and a green powder separated, which is probably sulphide of chromium. (Kemp.) The compound violently decomposes terchloride of phosphorus and dichloride of sulphur, with evolution of a large quantity of vapour and precipitation of the rose-coloured, insoluble sesquichloride of chromium. If the vapour of chlorochromic acid is allowed to pass through a narrow tube into a vessel filled with the vapour of dichloride of sulphur, vivid combustion takes place, and the rose-coloured powder is deposited. (Kemp.) In ammoniacal gas the compound solidifies with brilliant incandescence, forming a dark brown mass, which remains red-hot for some time. (Thomson.) The tube in which the ammoniacal gas is made to act on the substance, exhibits a purple-red glow for a long time. If more ammoniacal gas is passed over the ignited residue, it changes to a black powder. (Liebig, *Pogg.* 21, 359.) This substance is nitride of chromium. (Schrötter.) According to Persoz (*Ann. Chim. Phys.* 44, 323), the mass saturated with ammonia is a compound of 79·1 per cent. of terchloride of chromium, and 20·9 of ammonia.

Mercury acts violently on chlorochromic acid. (Dumas, Walter.) When olefiant gas is passed through this compound, it rises in temperature, evolves vapours of oil of olefiant gas, becomes opaque and brown, and is finally converted into a dark brown powder, which appears to be $CrCl^2$. The powder deliquesces in the air, forming a greenish brown liquid, from which ammonia precipitates a greenish brown oxide, while chromate of ammonia remains in the solution. If air is admitted at the same time with the olefiant gas, combustion ensues, the whole mass becomes ignited, and is converted into green chromic oxide, while dense fumes are given off. (Wöhler, *Pogg.* 13, 297.) If the compound is introduced in a basin into olefiant gas previously set on fire, continuous combustion ensues, without any separation of carbon. (Kemp.) With absolute alcohol, the compound generally evolves sufficient heat to produce combustion, attended with formation of heavy hydrochloric ether (C^4H^5Cl) and a green solution of sesquichloride of chromium. (Wöhler, Thomson.) A small quantity of the compound mixed with absolute alcohol sets it on fire, with explosion and violent projection of the liquids. (Walter.) Oil of turpentine is likewise inflamed by the compound, and wood-spirit, camphor, and olive oil, are rapidly decomposed. (Thomson, *Phil. Transact.* 1827; also *Pogg.* 31, 607.) Charcoal and indigo do not affect it. (Dumas, Thomson.) The compound sinks in water, and dissolves with evolution of heat sufficient to produce ebullition; the solution is found to contain chromic and hydrochloric acids. (Dumas, Walter.)

Chlorochromic acid dissolves iodine without being decomposed. (Walter.) It absorbs chlorine gas in abundance at ordinary temperatures, forming with it a brown, almost solid mass, which, when exposed to the air, emits dense reddish fumes having the odour of iodine. It dissolves in water with a hissing noise, and gives off its excess of chlorine. (Dumas.)

E. Aqueous Hydrochlorate of Chromic Acid.—1. Formed by dissolving chlorochromic acid in water.—2. By decomposing chromate of lead or silver at ordinary temperatures with excess of hydrochloric acid. Brown uncrystallizable liquid which dissolves gold; when heated, it evolves chlorine and is converted into sesquichloride of chromium. (Moser.) When evaporated, it gives off reddish yellow vapours, and leaves a brownish black, shining, uncrystallizable mass. (Berzelius.)

Chromium and Fluorine.

¶ A. Protofluoride of Chromium.—Greenish precipitate, which leaves the supernatant liquid nearly colourless. (Moberg.) ¶

B. Sesquifluoride of Chromium and Hydrofluate of Chromic Oxide.—1. By dissolving chromium or the hydrated sesquioxide in aqueous hydrofluoric acid, a green solution is obtained, which, on evaporation, leaves a green crystalline mass, perfectly soluble again in water.—

¶ 2. According to Moberg, sesquichloride of chromium gives a green precipitate with fluoride of potassium. ¶ Sesquifluoride of chromium unites with more basic metallic fluorides, forming grass green, pulverulent compounds, which, for the most part, are very sparingly soluble in water, but generally speaking, do not separate from the mixed aqueous solutions without the application of heat. (Berzelius.)

C. The brown hydrated sesquioxide yields with aqueous hydrofluoric acid a rose-coloured solution which dries up to a rose-coloured salt; this salt redissolves completely in water, and gives a brown precipitate with ammonia. (Berzelius, *Pogg.* 1, 34.)

D. TERFLUORIDE OF CHROMIUM.—A mixture of one part of chromate of lead with one part of fluorspar and 3 parts of fuming oil of vitriol is distilled in a tubulated leaden retort, and the vapours collected in a leaden receiver attached to the retort. (Unverdorben.) Instead of chromate of lead, bichromate of potash may also be used. (H. Rose.) According to Dumas (*Ann. Chim. Phys.* 31, 435), the vapours may be condensed by the application of cold.

Red vapour, the inhalation of which produces severe oppression of the lungs. (Unverdorben.)

The vapour is decomposed by water, with rise of temperature, into hydrofluoric and chromic acids. Hence, when exposed to the air, it evolves finely crystallized chromic acid in the form of a red and subsequently of a yellow cloud; it likewise imparts a coating of chromic acid to moist porous substances, which, when they are of organic nature, sometimes become green by deoxidizing the chromic acid. Silica, even as it exists in glass, converts terfluoride of chromium into gaseous fluoride of silicium and chromic acid. Consequently, on distilling the above-mentioned ingredients in a glass retort, fluoride of silicium is obtained, and chromic acid (containing hydrofluoric acid, however) sublimes into the neck of the retort. Boracic acid decomposes this compound, forming fluoride of boron and chromic acid; and arsenious acid converts it into fluoride of arsenic and chromic acid. Mercury decomposes the vapour very slowly, forming a pulverulent substance. Organic bodies are destroyed by the vapour, which combines with their hydrogen and oxygen; alcohol and ether, under these circumstances, produce hydrofluate of chromic oxide. (Unverdorben.) The vapour passed into absolute alcohol deposits large quantities of a brownish green powder with emission of heat. (Wöhler.) Terfluoride of chromium combines with ammonia. (Unverdorben.)

CrF^3 should contain in 100 parts: Chromium 33·29, Fluorine 66·71. H. Rose, however, by slowly passing the vapour into water and estimating the quantities of chromic and hydrofluoric acid produced, found the proportion of chromium to fluorine, in one experiment, = 24·73 : 75·27; and in a second, = 26·41 : 73·59. At the same time he observed that the vapour was not entirely absorbed, but that oxygen gas remained, and further, that sulphates of the green and brown oxide of chromium were present in the retort, besides sulphate of potash and sulphate of lime. This deviation of the analysis from the calculation may be explained in two different ways: 1. The pure compound is really CrF^3, but its vapour is mixed with oxygen gas and hydrofluoric acid vapour, the latter being evolved in the free state by the action of the hydrated oil of vitriol on the fluorspar. When this gaseous mixture is passed into water, the latter absorbs variable quantities of HF, in addition to the CrF^3, and consequently the analysis of this liquid gives an excess of fluorine.—2. The compound is CrF^5, which in 100 parts amounts to Cr 23·04 + F 76·96. This CrF^5 would be decomposed with 5HO, into $CrO^3,5HF$, and 2O; whence, in the absorption of the vapour by water, free oxygen gas must be left behind. [The presence of this gas, however, has already been sufficiently explained by the formation of chromic oxide in the residue of the distillation.] H. Rose regards the latter view as the more probable, because the excess of bichromate of potash must prevent the disengagement of hydrofluoric acid. Berzelius declares himself, with reason, in favour of the former theory.

E. HYDROFLUATE OF CHROMIC ACID.—The yellowish brown solution obtained by decomposing the terfluoride of chromium by water. This solution, when evaporated, gives off the hydrofluoric acid,—the greater part, according to Unverdorben; the whole, according to Berzelius. Zinc, tin, and other metals convert it into hydrofluate of chromic oxide and separate the oxygen.

CHROMIUM AND NITROGEN.

A. NITRIDE OF CHROMIUM.—Liebig (*Pogg.* 21, 359), by igniting sesquichloride of chromium in ammoniacal gas, obtained a brown powder, which he regarded as chromium. Schrötter described it as nitride of chromium. It is prepared by passing dry ammoniacal gas over sesquichloride of chromium heated in a glass tube. (Liebig, Schrötter.) To obtain the sesquichloride as free as possible from sesquioxide and water, it is previously heated in the glass tube in an oil bath, and a current of hydrochloric acid gas passed over it till no more water is evolved; the tube is then cooled, and ammoniacal gas passed through it for a long time; after which heat is applied, and the current of ammoniacal gas kept up till no more sal-ammoniac is sublimed. The mass, when cold, is removed from the tube, crushed, and again treated with ammonia, the whole process being repeated several times. (Schrötter.) When chlorochromic acid is treated in the same way with ammonia, a black nitride of chromium is obtained, probably of similar composition. (Schrötter.)

$$3(Cr^2Cl^3) + 13NH^3 = 2Cr^3N^2 + 9(NH^4Cl) + 3H.$$

Brown powder. (Liebig, Schrötter.) Inflames in a current of oxygen gas at a temperature between 150° and 200°, burning with a red light, and evolving nitrogen gas and a small quantity of hyponitric acid vapour; the residue is sesquioxide of chromium. (Schrötter, *Ann. Pharm.* 37, 148.)

	Calculation.		Schrötter.
3Cr	84	75	76·32
2N	28	25	
Cr^3N^2	112	100	

[Schrötter found that 562 parts of nitride of chromium heated in a current of oxygen gas yielded on the average 612·74 parts of chromic oxide. In these 612·74 parts, Schrötter supposed, from an error in calculation, that only 359·47 parts of metallic chromium were present (there being in reality 429). Accordingly, he concluded that 562 parts of nitride of chromium contain 359·47 (4 atoms) of chromium, and 202·53 parts (5 atoms) of nitrogen, corresponding to the formula Cr^4N^5.]

B. Nitrate of Chromic Oxide.—Prepared by dissolving the hydrated sesquioxide in nitric acid. The solution is blue by reflected, and red by transmitted light. Has a sweet, astringent taste; does not yield crystals on evaporation, but dries up to a gummy, fissured mass, which appears dark green both by reflected and transmitted light. After exposure for several hours to the heat of a water-bath, it dissolves partially in water, yielding a brown solution. (Hayes.)

C. Brown Nitrate of Chromium.—If the green chromic nitrate is evaporated to dryness, and gently calcined, it swells up, evolves nitrous acid vapours, and turns brown; after this, it forms a brownish red solution in water. (Berzelius.) The yellow solution of the brown hydrated oxide in nitric acid of specific gravity of 1·18 leaves, when evaporated at a gentle heat, a blackish brown mass, which becomes moist in the air and dissolves completely in water. (Brandenburg.)

D. Nitrate of Chromic Acid.—Formed by mixing nitric acid with chromic acid, or by precipitating a solution of chromate of baryta in nitric acid, with the exact quantity of sulphuric acid required, and filtering the liquid. On evaporating the solution, a brownish red or yellowish red crystalline powder is obtained, having a very acid and rough taste. This powder fuses when heated, and is converted first into brown nitrate of chromium, and lastly into the green oxide. With oil of vitriol it gives off nitric acid fumes, whereby it is distinguished from pure chromic acid. Deliquesces in the air; yields a brown solution with a small quantity of water, and a yellow solution with a larger quantity. (Brandenburg.) When a solution of chromate of potash, likewise containing nitre, such as that obtained in the treatment of chrome-iron ore (p. 108) is precipitated by a salt of baryta, the chromate of baryta which separates contains a portion of nitric acid intimately combined, and therefore, when decomposed by dilute sulphuric acid—even without being dissolved in nitric acid—yields chromic acid containing nitric acid. (Brandenburg, Meissner, Moser.) Richter, by precipitating chromate of potash with nitrate of silver, and decomposing the precipitate by a quantity of hydrochloric acid insufficient for complete saturation, likewise obtained a chromic acid containing nitric acid; because chromate of silver, according to Brandenburg and Moser, likewise combines intimately with nitric acid. According to Brandenburg, and Meissner also, the precipitate produced in chromate of potash by nitrate of lead contains traces of nitric acid.

E. Chromic Oxide and Ammonia.—*Chromate of Ammonia.*—*a.* If a salt of chromic oxide is mixed with an excess of ammonia, a portion of the precipitated oxide dissolves in the ammonia, even when kept out of contact of air, and forms a peach-blossom coloured or columbine-red solution. The more concentrated the ammonia and the greater its excess, the larger is the quantity of oxide dissolved. It dissolves much more abundantly when the chromium-salt is dropped into the ammonia than in the contrary case, because the oxide, at the moment of its separation from the acid, is taken up by the ammonia. Under favourable circumstances, 0·4 per cent. only of the chromic oxide remain undissolved. It appears that the chromic oxide must first be converted by the ammonia into a peculiar modification (from the green into the purple) before it can dissolve in the ammonia. If a solution of chrome-alum is evaporated with a small quantity of oil of vitriol to a small bulk, and the mixture dropped into an excess of ammonia, less than 0·2 per cent. of chromic oxide remains undissolved. The ammoniacal solution exposed to the air, deposits a violet-coloured hydrate, the solution of which in sulphuric acid becomes green on boiling. (Hertwig, *Ann. Pharm.* 45, 299.)

b. The precipitate produced by excess of ammonia in salts of chromic oxide, is not pure hydrated sesquioxide, but contains ammonia, even after prolonged washing with hot water: the ammonia may be liberated by potash.

This compound exhibits two modifications, according to the manner in which the ammonia acts in producing it.

α. Green Precipitate.—One measure of ammonia, of specific gravity 0·984, is added, drop by drop, to a saturated solution of chrome-alum. The precipitate is of a pale green colour. It does not change its colour after remaining three days in contact with the ammonia, unless the ammonia is in very large excess, in which case it is partially converted into *β*. Even after the digestion with ammonia, it yields with sulphuric acid a violet solution, which becomes green on boiling; the same solution, when saturated as nearly as possible with ammonia, without a precipitate being produced, assumes a grass-green colour; with a larger quantity of ammonia, and also with phosphate of soda, it gives a green precipitate. This is the same modification of chromic oxide as that which occurs in chrome-alum.

β. Violet Precipitate.—The solution of chrome-alum is dropped into ammonia—the same proportions being employed as in *α*—and the greyish violet precipitate (the solution of which in sulphuric acid is also violet, but becomes green on boiling) is kept for three days in contact with ammonia in a stoppered bottle, whereupon, a portion dissolves, forming a red solution. The undissolved portion of oxide is violet. A solution of the unwashed precipitate in sulphuric acid has a wine-red colour. With carbonate of soda it yields, after a while, a dark violet precipitate. It retains its wine-red colour when saturated as nearly as possible with ammonia; after which, on dilution with water, it deposits a rose-coloured precipitate. With phosphate of soda it gives a violet precipitate which turns green at the boiling-point. Ammonia in excess precipitates a violet-coloured hydrate containing ammonia. When boiled, the red solution becomes violet or green; after which, both ammonia and phosphate of soda throw down a blue precipitate. This red modification is also perfectly formed in the red ammoniacal solution of chromic oxide.

When the green or violet precipitate *α* or *β* is freed by washing and drying from the greater part of the ammonia which produced that modification, *α* dissolves at once in sulphuric acid, forming a green solution, and *β* a violet solution; but the latter also turns green on boiling. The same change is effected by boiling the violet precipitate *β* in the ammoniacal liquid from which it is precipitated—so that it yields with sulphuric acid a violet solution which turns green on boiling. (Hertwig.)

F. CHROMATE OF AMMONIA.—*a. Monochromate.*—Prepared by evaporating a mixture of chromic acid with a slight excess of ammonia. Crystallizes in lemon-yellow needles, having an alkaline reaction and a pungent saline taste; they are permanent in the air, and very soluble in water. When heated, they retain a portion of the ammonia, till they are entirely converted into chromic oxide; and their aqueous solution, after repeated evaporation, readily deposits portions of brown oxide. (Vauquelin, Richter, Moser.) When rapidly heated till decomposition takes place, the salt exhibits incandescence, and is converted into the green sesquioxide; if the temperature is slowly raised, the decomposition is not attended with emission of light and heat, but nevertheless takes place suddenly throughout the whole mass, an oxide being left which dissolves in concentrated acids with tolerable facility. (Maus.)

	Crystallized and dried over oil of vitriol.			Kopp.
NH^3	17	....	21·79	
CrO^3	52	....	66·67	66·3
HO	9	....	11·54	
NH^3, HO, CrO^3	78	....	100·00	

b. Bichromate.—Crystalline system, the oblique prismatic. *Fig.* 86; with the i-face frequently rounded off; $i : u$ or $u^1 = 114°$; $i : h = 110° 10'$; $i : f$ (*backwards*) $= 101° 58'$; $i : m = 122° 31'$; $u^1 : u = 98° 8'$; $u : m = 139° 4'$; $u : h = 135° 47'$; cleavage parallel to m and t. (Brooke, *Ann. Phil.* 22, 287.) Forms orange-yellow plates, which redden litmus, have a saline taste, are permanent in the air, and less readily soluble in water than *a*. (Moser.) The salt crystallizes in reddish-brown, rhombic prisms, which, at a temperature below redness, are decomposed with emission of light and feeble detonation, leaving a residue of chromic oxide. (Hayes.)

¶ Darby has analyzed this salt, prepared by partially saturating chromic acid with ammonia, and evaporating to the crystallizing point, and finds that it contains NH^3, combined with the 2 equivalents of chromic acid, instead of NH^4O, as in the monochromate. (*Ann. Pharm.* 65, 204.) ¶

	Calculation.				Darby.	
NH^3	17·0	....	14·05			
$2CrO^3$	104·0	....	85·95	....	84·96	85·2
$NH^3, 2CrO^3$	121·0	....	100·00			

G. Carbonate of Chromic Oxide and Ammonia.—Carbonate of chromic oxide dissolves very sparingly in an aqueous solution of carbonate of ammonia, forming a pale greenish-blue solution.

H. *Tersulphide of Chromium with Hydrosulphate of Ammonia?*—Chromic acid yields with very dilute bi-hydrosulphate of ammonia a brown solution which contains the sulphur-salt, and at the same time a greyish-green precipitate, which, after being washed and dried, behaves like a mixture of hydrated chromic oxide and sulphur,—but at the moment of its formation, dissolves in potash (not in ammonia, or bi-hydrosulphate of ammonia), forming a green solution, and leaving a residue of hydrated sesquioxide. With acids, the solution evolves sulphuretted hydrogen and deposits sulphur, while a salt of chromic oxide remains dissolved. (Berzelius.)

I. Sulphate of Chromic Oxide and Ammonia.—*Ammonia Chrome-alum.*—Prepared by mixing tersulphate of chromic oxide with ammonia. (Mitscherlich.)—If sulphate of ammonia is added to a concentrated solution of the blue crystallized tersulphate of chromic oxide (p. 127), the double salt is immediately precipitated in the crystalline form; it is purified by a second crystallization after the removal of the mother-liquid. (Schrötter.)

Regular octohedrons (Mitscherlich), having likewise the faces of the cube and dodecahedron. Specific gravity 1·736 at 21°. (Schrötter.) Cleavage indistinct, parallel to the octohedral faces. Fracture conchoidal, with a vitreous lustre. Colour brilliant violet-blue, passing into columbine-red (ruby-red by transmitted light, *Schrötter*). Streak, very pale lavender-blue. Slightly transparent. Taste, slightly sweetish and saline. (Hardinger, *Edinb. J. of Sc.* 1, 100.)

	Calculation.		Schrötter.
NH^3	17	3·53	
Cr^2O^3	80	16·59	16·26
$4SO^3$	160	33·20	33·10
25HO	225	46·68	
$NH^3,HO,SO^3 + Cr^2O^3,3SO^3 + 24Aq.$	482	100·00	

The salt effloresces superficially in the air, and becomes covered with a pearl-grey powder. Fuses at 100°, forming a green liquid which shows no signs of dichroism; 18 atoms of water are evolved at the same time. On cooling, the salt solidifies in a pale green mass, which does not part with the remaining portion of water till it is heated to above 300°. —It dissolves in cold water, forming a blue solution, which at 75° or 80° assumes a grass-green colour, because the alum is decomposed at that temperature;—so that the solution yields no more crystals on evaporation, but dries up to a green mass, and is moreover no longer precipitated by alcohol, but either mixes with it, or, when concentrated, forms a substratum, the alcohol floating on the surface. But if the solution, after being turned green by heat, is diluted with water, and left to stand for ten days, the alum is gradually reproduced. Alcohol precipitates the alum from its solution in water. (Schrötter, *Pogg.* 53, 526.)

When a solution of the blue crystallized tersulphate of chromic oxide is mixed with excess of sulphuric acid, then treated with alcohol, and the green solution decanted from the precipitated blue salt, and mixed with so much ammonia that it still remains slightly acid, a dark green, highly acid solution separates to the bottom; and subsequently, after long standing, the liquid becomes decolorized, and a light green salt is deposited, which, for every 14 atoms of sulphate of ammonia, contains one atom of chromic oxide in combination with 6 atoms of sulphuric acid and 33 atoms of water. (Schrötter.)

K. *Ammonio-terfluoride of Chromium*—Ammoniacal gas condenses, according to Unverdorben, with fluoride of chromium, forming a yellow powder, which sublimes without decomposition. According to Berzelius, however, the vapour of fluoride of chromium explodes with ammoniacal gas, the products being nitrogen and hydrofluoric acid.

L. Sesquifluoride of Chromium + Hydrofluate of Ammonia. —Green, sparingly soluble powder. (Berzelius.)

M. Chromate of Sal-ammoniac.—Formed by adding chlorochromic acid to a concentrated solution of sal-ammoniac. The crystals have the same form and appearance as the corresponding potassium compound, but are much more soluble in water. (Peligot, *Ann. Chim. Phys.* 52, 267; also *J. Pharm.* 19, 301; also *Ann. Pharm.* 8, 1.)

	Calculation.		Peligot.
NH^3	17·0	10·80	10·8
HCl	36·4	23·13	23·5
$2CrO^3$	104·0	66·07	65·5
$NH^3, HCl, 2CrO^3$	157·4	100·00	99·8

Chromium and Potassium.

A. Chromic Oxide and Potash.—*Chromite of Potash.*—A cold aqueous solution of potash dissolves hydrated chromic oxide, forming a grass-green solution. This liquid, unless it contains a large excess of potash, deposits a jelly after some time, leaving the supernatant liquid colourless; when heated to the boiling point, it also becomes colourless, green flakes being precipitated. According to Moser, however, a small quantity of chromate of potash, produced by the action of the air, remains dissolved. Boudault (*Ann. Pharm.* 59, 351) has observed that a solution of chromic oxide in potash is converted into chromate of potassh by the addition of ferricyanide of potassium.

The brown hydrated oxide dissolves in aqueous potash, forming a brown solution.

B. Chromate of Potash.—*a. Monochromate.*—1. Prepared by either of the methods given for the preparation of chromic oxide (p. 108). When this salt is present in solution, together with bichromate of potash and nitre, the latter salts crystallize out first on the addition of nitric acid. By the addition of potash, the bichromate may be converted into the normal salt, and separated from the nitre either by crystallization, or by fusion and the cautious addition of charcoal powder, till the violent detonation ceases; the mobile liquid then becomes pasty, and a small quantity of chromic oxide is separated; the mass is then exhausted with water, the solution filtered, and left to crystallize. (Tassaert.)—2. By neutralizing commercial bichromate of potash with carbonate of potash. (Thomson; Liebig & Wöhler.)—3. By projecting chromic oxide into fused chlorate of potash. (Liebig & Wöhler, *Pogg.* 24, 171.) —The commercial salt frequently contains sulphate of potash. In this case the solution must be supersaturated with nitric acid and precipitated by nitrate of baryta. To obtain the commercial salt perfectly pure, it is freed by recrystallization from silica and alumina, then mixed with nitric acid, and nitrate of baryta dropped in as long as sulphate of baryta is precipitated. Chromate of silver is then added to the filtrate as long as chloride of silver is formed; after which the solution is filtered, evaporated to dryness, and the residue ignited in a platinum crucible; lastly the residue is dissolved in water, and the solution left to crystallize. (Hayes, *Sill. Amer. J.* 20, 409.)

Crystalline system the right prismatic; isomorphous with monosulphate of potash. *Fig.* 77; excepting that the faces between a and t are wanting. $n : n = 110^\circ\ 10'$; $y : y$, *backwards* $= 120^\circ\ 41'$; cleavage parallel to m and t. (Mitscherlich, *Pogg.* 18, 168.) $u' : u = 72^\circ\ 34'$; $a : u = 133^\circ\ 52'$; $u : m = 126^\circ\ 17'$; $y : m = 119^\circ\ 43'$; $y : y$, *backwards* $= 120^\circ\ 34'$; the faces m and i being the broadest. (Brooke, *Ann. Phil.* 22, 120.)—Sp. gr. = 2·6115 (Thomson), = 2·6402 (Karsten), = 2,705 (Kopp). Lemon-yellow; assumes an aurora-red tint whenever it is heated. Up to 204°, it undergoes no further change. Fuses at a red heat, previous to which it decrepitates violently. According to Berzelius, it emits a green light during fusion, and, according to Magnus, crystallizes as it solidifies on cooling. Has an alkaline reaction, and a cooling, persistently bitter and metallic taste. Permanent in the air.

	Crystallized.		Tassaert.	Thomson.
KO	47·2	47·58	48	48
CrO^3	52·0	52·42	52	52
KO, CrO^3	99·2	100·00	100	100

When ignited alone it is not decomposed. By strong ignition with charcoal, it is resolved into carbonate of potash and chromic oxide. (Moser.)—It is likewise partially decomposed by ignition in a current of carbonic oxide, sesquioxide of chromium being separated. (Göbel.)—Charcoal, cotton wool, and other organic substances, burn with greater rapidity when saturated with its solution and dried. (Jacobson.)—When ignited with sulphur, it is resolved into chromic oxide, sulphate of potash, and sulphide of potassium. (Lassaigne.) Probably in the following manner:

$$8(KO,CrO^3) + 20S = 5(KO, SO^3) + 3KS^5 + 4Cr^2O^3.$$

According to Döpping, however, if the mixture be gently heated, hyposulphite of potash is likewise formed at the beginning of the action, but is again partially decomposed by the heat evolved, in consequence of the combination of the oxygen of the chromic acid with the sulphur.

An aqueous solution of the salt, when heated with pentasulphide of potassium, yields a gelatinous precipitate of hydrated chromic oxide, together with hyposulphite of potash and free potash. (Döpping, *Ann. Pharm.* 46, 172.)

$$8(KO, CrO^3) + 2KS^5 = 5(KO, S^2O^2) + 5KO + 4Cr^2O^3.$$

With arsenious acid (or an arsenite) the solution gradually forms a green liquid, (Cooper, *Ann. Phil.* 20, 77), which solidifies after some minutes to a stiff jelly; but if the potash salt be added to the arsenious solution, a green colour is produced without precipitation. (Schweitzer, *J. pr. Chem.* 39, 267.) Sulphurous acid passed through the aqueous solution, precipitates brown hydrated oxide of chromium, which, however, gradually turns green, and then dissolves completely, forming a green solution containing potash, chromic oxide, sulphuric acid, hyposulphuric acid, and sulphurous acid. When boiled, it evolves sulphurous acid, and deposits the whole of the chromium in the form of basic sulphite of chromic oxide. (Berthier, *N. Ann. Chim. Phys.* 7, 77.) By heating with acetic acid and alcohol, the salt is partially converted into acetate of potash and acetate of chromic oxide. (Tassaert.) It gives up the whole of its chromic acid to baryta-water. (Döbereiner.) To many acids, as the sulphuric, hydrochloric, nitric, and acetic, it gives up half of its potash, and is thereby converted into bichromate, which separates after slight concentration. (Tassaert.) A solution of the salt in hot hydrochloric acid, deposits crystals of chloride of potassium on cooling; a solution in a hot mixture of hydrochloric and sulphuric acid yields chrome-alum. (Marchand, *Pogg.* 45, 594.)

Chromate of potash dissolves, according to Thomson, in 2·07 parts of water at 15·5° (60° F.); according to Moser, in 1·75 parts at 17·5°, and in 1·67 parts at 100°. When the salt is dissolved in 2 parts of water, the temperature falls about 10°. A solution of one part of salt in 2 parts of water, has a specific gravity of 1·28; in 3 parts of water, 1·21; in 4 parts, 1·18; in 5 parts, 1·15; in 6 parts, 1·12; in 7 parts, 1·11; and in 8 parts, 1·10. (Moser.) Sp. gr. of a saturated solution at 8° = 1·368. (Anthon.) One part of the salt imparts a distinct yellow colour to 40,000 parts of water; it likewise imparts to 20 parts of nitre a fine lemon-yellow colour, when the salts are allowed to crystallize together. (Thomson.) Chromate of potash is insoluble in alcohol, which precipitates it also from an aqueous solution. According to Thomson, tincture of galls precipitates the solution brown.

When chromic acid is mixed with potash in such proportions that the aqueous solution is neither acid nor alkaline, and the mixture evaporated, bichromate of potash, having an acid reaction, crystallizes out first, and then the monochromate, which exhibits an alkaline reaction. (Tassaert.)

b. *Bichromate*.—When a solution of *a* is mixed with nitric acid, the salt *b* crystallizes out either immediately or after evaporation. The crystals are separated mechanically from those of nitre, and purified by recrystallization. (Tassaert.) Large, bright-red, rectangular, four-sided tables and prisms—or when more rapidly crystallized—thinner laminæ; its powder is reddish yellow. Sp. gr. = 1·98, (Thomson), = 2·6027 (Karsten.) Decrepitates in the fire; fuses at a heat considerably below redness, and much more readily than *a*, forming a transparent red liquid; on cooling it solidifies again in the form of a red fibrous mass, which falls to pieces spontaneously. (Thomson.) When slowly cooled after fusion, it yields fine large crystals, which have the same form as those obtained from an aqueous solution, but on further cooling, crumble to powder. (Mitscherlich, *Pogg.* 28, 120.) The salt has a cooling, bitter, and metallic taste, reddens litmus, and is permanent in the air. (Thomson.)

			Tassaert.	Thomson.	Grouvelle.
	Crystallized.			*Ignited.*	
KO	47·2	31·22	32·6	31·579	31·154
$2CrO^3$	104·0	68·78	67·4	68·421	68·846
$KO,2CrO^3$	151·2	100·00	100·0	100·000	100·000

At a white heat, half the chromic acid is decomposed, yielding oxygen gas and chromic oxide, while monochromate of potash remains behind. (Grouvelle.) Detonates slightly with charcoal. Three parts of bichromate of potash gently heated with 4 parts of oil of vitriol, are resolved into sulphate of chromic oxide and potash, together with water and oxygen gas. In this manner oxygen may be prepared pure, and more cheaply than from chlorate of potash. (Balmain, *Phil. Mag. J.* 21, 42; also II., 22.)

$$KO,2CrO^3+4(HO,SO^3)=(KO,SO^3+Cr^2O^3,3SO^3)+4HO+3O.$$

Hydrosulphuric acid gas passed through an aqueous solution of bichromate of potash, precipitates chromic oxide mixed with sulphur. (Hayes.) Sulphurous acid gas passed through the solution colours it green without precipitation, sulphate and hyposulphate of chromic oxide being produced. (Berthier.) A current of nitric oxide decomposes it, throwing down brown chromic oxide, or, after a while, metallic chromium. (p. 114.) From a solution of the salt in boiling hydrochloric acid, chromate of chloride of potassium crystallizes out as the liquid cools. (Peligot.) The salt dissolves in water with slight reduction of temperature. (H. Rose.) It dissolves in 9·6 parts of water at 17·2 (Thomson), and in 10 parts at 18·7°. (Moser.) The solution has a deep orange-yellow colour. According to Anthon, a solution saturated at 8°, has a specific gravity of 1·065. The salt is insoluble in alcohol.

According to Graham, there exists also a *Terchromate of Potash.*

C. Carbonate of Chromic Oxide and Potash.—Carbonate of chromic oxide dissolves sparingly in aqueous solution of carbonate of potash, forming a pale greenish-blue solution and separating again after long boiling. When sesquichloride of chromium is supersaturated with a concentrated solution of carbonate of potash, scarcely any of the precipitate is redissolved; solution takes place only on mixing more dilute solutions. The solution of hydrated carbonate of chromic oxide in boiling bicarbonate of potash deposits double carbonate of chromic oxide and potash in pale green crystalline scales as it cools; a solution in monocarbonate of potash yields a pulverulent double salt on evaporation. (Berlin.)

¶ D. Pyrophosphate of Chromic Oxide and Potash.—Known only in solution. The liquid exactly resembles sulphate of nickel in colour, and is not affected either by hydrosulphuric acid, or by hydrosulphate of ammonia. (Persoz, *Ann. Pharm.* 65, 163.) ¶

E. *Tersulphide of Chromium with Sulphide of Potassium?*—An aqueous solution of chromate of potash, saturated with hydrosulphuric acid, becomes dark brown and opaque, and yields a greyish-green precipitate of sesquisulphide of chromium. The filtrate deposits brown tersulphide of chromium on exposure to the air, and likewise on the addition of acids; but the precipitate is rapidly decomposed even in the liquid itself. When digested in the air, especially in a dilute state, sulphur is deposited, and chromate of potash formed. (Berzelius, *Pogg.* 8, 422.)

¶ F. Sulphate of Chromous Oxide and Potash.—Prepared by bringing protochloride of chromium in contact with a cold saturated solution of monosulphate of potash, adding alcohol till a slight precipitate appears, and then leaving the mixture at rest in a closely stoppered bottle for a week or two. By this process, very distinct blue crystals are obtained, having the form of rhombic prisms. They rapidly turn green in the air.

					Peligot.		
	Calculation.				(1)		(2)
CrO	36·0	....	16·57	....	16·6	....	17·0
KO	47·2	....	21·73				
$2SO^3$	80·0	....	36·83	....		....	37·0
6HO	54·0	....	24·87				
$KO,SO^3 + CrO,SO^3 + 6Aq$	217·2	....	100·00				

This salt appears to have the same composition as the numerous double sulphates formed with the oxides of the magnesia group; and, according to Prevostaye, is isomorphous with the double sulphate of ferrous oxide and potash. (Peligot.) ¶

G. Sulphate of Chromic Oxide and Potash.—$KO, SO^3 + Cr^2O^3, 3SO^3$.—*a. Anhydrous.*—*α. Not decomposible by water.*—A solution of potash-chrome-alum, converted into the green modification by heat, is evaporated to the consistence of syrup; warmed, after the addition of oil of vitriol, to a temperature of 200°, as long as water is evolved; and the resulting insoluble salt freed from the unaltered portion and from the excess of sulphuric acid, by washing with water. Light green powder. At a temperature below redness, it loses 5·8 per cent. of sulphuric acid, and at a strong red heat, the whole of the acid which is in combination with the chromic oxide; whereupon water dissolves out the sulphate of potash. The salt is decomposed by long boiling in solution of potash, with separation of green sesquioxide of chromium, which is not dissolved by hydrochloric acid till after long boiling. Ammonia, water, sulphuric acid, hydrochloric acid, and nitric acid, neither decompose nor dissolve this compound, even when boiled with it. (Hertwig, *Pogg.* 56, 95.)

	a. Dried at 100°.			Hertwig.
KO	47·2	....	16·43	
Cr^2O^3	80·0	....	27·85	27·325
$4SO^3$	160·0	....	55·72	55·516
	287·2	....	100·00	

β. *Decomposible by water.*—Formed by heating potash-chrome-alum between 300° and 400°, till the water is entirely driven off. Light green. When boiled for a long time with water (cold water has no action), it is resolved into soluble sulphate of potash and sulphate of chromic oxide (p. 126, *c. α.*) which remains in the form of an insoluble green powder. (Hertwig.)

b. Bihydrated.—First observed by Fischer.—Prepared by keeping potash-chrome-alum at a temperature of 200° as long as it continues to lose water; the quantity expelled amounts to 39·522 per cent. = 22 atoms. The residue is a dark green porous mass. It is decomposed by warm aqueous ammonia, which separates a dark green oxide soluble in boiling hydrochloric acid. It dissolves when boiled for a long time with water, more rapidly, however, if hydrochloric acid is added. Water and dilute sulphuric or hydrochloric acid do not act on the double salt at ordinary temperatures, at least in the course of several days. (Hertwig.)

c. With 24 *atoms of water.*—*Potash-chrome-alum.*—First obtained by Mussin-Pouschkin. (*Crell. Ann.* 1801, 2, 267.)—1. An aqueous solution of the blue crystallized tersulphate of chromic oxide and sulphate of potash, is mixed with sulphuric acid and left to evaporate spontaneously. (Berzelius.)—2. Through an aqueous solution of one atom of bichromate of potash and one atom of oil of vitriol, sulphurous acid gas is passed as long as it continues to be absorbed, the vessel containing the mixture being artificially cooled, to prevent the liquid from becoming too much heated:

$$KO,2CrO^3 + SO^3 + 3SO^2 = KO,SO^3 + Cr^2O^3,3SO^3.$$

(Schrötter, *Pogg.* 53, 326.)—3. One part of oil of vitriol is added to 3 parts of a saturated aqueous solution of monochromate of potash, and, after the bichromate of potash which separates is redissolved, 2 parts of alcohol are added by small portions at a time, so as to prevent too great a rise of temperature. The mixture after some time assumes a green colour and deposits crystals of chrome-alum. These crystals are redissolved in a fresh quantity of water, and the solution poured into shallow dishes and left to evaporate spontaneously. The crystals thus obtained are dried between blotting paper, and freed from sulphate of chromic oxide and bisulphate of potash by washing them with a small quantity of cold water, till the liquid which runs off is no longer green but violet. (Fischer, *Kastn. Arch.* 14,164; 16,212.) By using strong oil of vitriol a large proportion of the chromic oxide is converted into the green modification, which does not yield any chrome-alum: with dilute sulphuric acid, on the contrary, the decomposition takes place slowly, and without perceptible rise of temperature, and the whole of the chromic oxide crystallizes out as alum. (Berzelius.) ¶ Traube, (*Ann. Pharm.* 66, 165), gives the following improved method. One part of bichromate of potash is dissolved in 2 parts of sulphuric acid diluted with a quantity of water sufficient to prevent the solution from depositing crystals at ordinary temperatures; the whole is then gradually added to a quantity of alcohol contained in a vessel which is surrounded with cold water, to prevent too great a rise of temperature. A considerable portion of the chrome-alum is at once precipitated in the form of a crystalline meal. The mother-liquid is then mixed with $\frac{1}{7}$ of its weight of nitric acid, to prevent the formation of the green modification; evaporated in a water bath to $\frac{1}{4}$ its weight; and lastly treated with an equal weight of alcohol, and set aside to crystallize. The greater part of the remaining chrome-alum separates in crystals, which are purified by recrystallization from a solution in water heated to 50°. ¶

Chrome-alum forms regular octohedrons of a violet-red colour, ruby-red by transmitted light; it is permanent in the air. When impure, however, it effloresces on the surface, assuming a green colour if it contains excess of chromic sulphate, and a violet colour if the sulphate of potash predominates. (Fischer.)

	Calculation.			Fischer.
KO	47·2	.... 9·38	....	9·52
Cr^2O^3	80·0	.... 15·90	....	15·60
$4SO^3$	160·0	.... 31·80	....	32·27
24HO	216·0	.... 42·92	....	42·60
$KO,SO^3 + Cr^2O^3,3SO^3 + 24Aq.$	503·2	.... 100·00	....	99·99

¶ According to Jacquelain (*Compt. rend.* 24, 439) chrome-alum contains only 22 atoms of water. ¶

When heated, it fuses, gives off its water of crystallization, and is converted into the grass-green coloured salt *b* (Fischer), and at a temperature between 300° and 400°, into the salt *a*, (Hertwig); lastly, it is converted by ignition into a powder which is lilac-coloured while hot, and yellowish-green when cold. This powder is perfectly insoluble in boiling water and in all acids, except oil of vitriol, which dissolves it in very small quantity, and deposits it again for the most part on cooling, or completely on the addition of water. (Fischer.) [This is probably the salt *a*, *α*.]

Chrome-alum is soluble in 6 parts of cold water; the violet solution suffers the alum to crystallize out unchanged by spontaneous evaporation; but if heated to between 50° and 75°, it turns green, and according to the extent of decomposition, either deposits, on evaporation, a brilliant green, amorphous, difficultly soluble mass, or yields crystals of sulphate of potash, leaving green sulphate of chromic oxide in solution. (Fischer.) The sulphate of potash separates only from a highly concentrated solution, and in small quantity. (Schrötter.) A solution which has been turned green by boiling, becomes blue again after long standing, and when evaporated yields crystals of chrome-alum, with which a small quantity of the green salt still remains mixed. By re-solution and standing, the latter is also converted into chrome-alum. These changes are similar to those exhibited by blue and green sulphate of chromic oxide. Chrome-alum contains the blue sulphate; a solution of chrome-alum introduced into a glass tube, and covered with a stratum of alcohol, likewise yields a result similar to that described on page 127. (Schrötter.)

H. Sulphate of Potash with Chromate of Potash.—*a.*—*With Monochromate of Potash.*—Sent into the market by French manufacturers instead of the pure monosulphate. It crystallizes in pale yellow, four and six-sided prisms, with four or six-sided summits; has a bitter taste; and decrepitates on ignited charcoal. Contains 43·3 per cent. of chromate, and 56·7 of sulphate of potash. With nitrate of baryta it gives a precipitate, which dissolves but partially in nitric acid, sulphate of baryta being left behind. Dissolves with great facility both in cold and in hot water; from the latter solution it crystallizes on cooling. (Boutron-Charlard, *J. Pharm.* 9, 184.)

b. With Bichromate of Potash.—If in the preparation of chromic acid by Fritzsche's method (p. 117) a slight excess of chromate of potash is used, and the precipitated red acid is dissolved in a small quantity of cold water, a yellow salt remains, which crystallizes from a solution in warm water, in broad rhombic needles, united together in stellated masses. The salt is of a yellowish-red colour, somewhat lighter than that of bichromate of potash, which it resembles in taste. When heated it becomes deep red, loses a small quantity of water, and then fuses to a dark brown liquid, solidifying, as it cools, in a metallic-looking mass, which assumes a liver-colour in the air. (Reinsch, *J. pr. Chem.* 28, 371.)

	Calculation.		Reinsch.
$\mathrm{2KO}$	94·4	39·60	
$\mathrm{2CrO^3}$	104·0	43·62	38·64
$\mathrm{SO^3}$	40·0	16·78	16·21
$\mathrm{KO,SO^3 + KO,2CrO^3}$	238·4	100·00	

I. Chromate of Chloride of Potassium.—1. An aqueous solution of bichromate of potash is boiled for a short time with excess of hydrochloric acid and left to crystallize by cooling:

$$\mathrm{KO,2CrO^3 + HCl = KCl,2CrO^3 + HO.}$$

If the boiling be too long continued, the chromic acid and the excess of hydrochloric acid re-act upon each other in such a manner as to yield chromic oxide and chlorine.—2. An aqueous solution of one atom of chloride of potassium acidulated with hydrochloric acid, is added to an aqueous solution of 2 atoms of chromic acid.—3. Chromate of chloride of chromium is treated with a saturated solution of chloride of potassium:

$$\mathrm{3KCl + 2(CrCl^3,2CrO^3) + 6HO = 3(KCl,2CrO^3) + 6HCl.}$$

The crystals are dried between folds of blotting paper.

The salt forms right rectangular prisms which have the same colour as bichromate of potash, and are transparent and permanent in the air. When treated with oil of vitriol, it evolves terchloride of chromium; [or rather chlorochromic acid;] probably thus:

$$\mathrm{3(KCl,2CrO^3) + 12SO^3 = 3(KO,SO^3) + CrCl^3,2CrO^3 + 3(CrO^3,3SO^3).}$$

The salt becomes white and opaque in pure water, and dissolves, forming a solution, which, when evaporated, either spontaneously or with the aid of heat, deposits crystals of bichromate of potash, hydrochloric acid being set free; but from a solution in water containing hydrochloric acid, the chromate of chloride of potassium crystallizes out undecomposed. If the water contains only a small quantity of hydrochloric acid, bichromate of potash separates at the same time with the chromate of chloride of potassium; with too much hydrochloric acid, a portion of the chromic acid is converted into chromic oxide. (Pelouze, *Ann. Chim. Phys.* 52, 267.)

	Calculation.			Pelouze.
K	39·2	21·95		21·88
Cl	35·4	19·82		19·41
$2CrO^3$	104·0	58·23		58·21
$KCl, 2CrO^3$	178·6	100·00		99·50

K. SESQUIFLUORIDE OF CHROMIUM + FLUORIDE OF POTASSIUM.—Green powder, very difficultly soluble in water. (Berzelius.)

L. *Bichromate of Potash + Nitrate of Potash?*—The yellow solution of bichromate of potash in nitric acid turns dark brownish-red when boiled, but becomes somewhat paler again on cooling, and, after the greater part of the nitric acid has been evaporated, leaves a thick, black, uncrystallizable liquid; when further heated, it continues to evolve strong nitric acid, then solidifies, gives off hyponitric acid gas, and is reconverted into bichromate of potash. (Reinsch.)

CHROMIUM AND SODIUM.

A. CHROMITE OF SODA.—Similar to the potash compound.—On platinum, chromic oxide forms with carbonate of soda in the inner blowpipe flame, an opaque glass, which appears green when cold. In the outer flame, a dark yellowish-brown glass is obtained, which becomes yellow and opaque on cooling.

B. CHROMATE OF SODA.—*a. Monochromate.*—1. Formed by igniting chrome-iron ore with half its weight of hydrate of soda and a small quantity of nitrate of soda, exhausting the fused mass with water, and leaving the solution to crystallize. (Moser.)—2. By neutralizing chromic acid with carbonate of soda. (Moser.)—3. By igniting one part of chromic oxide with 2 parts of nitrate of soda, digesting the mass in water, filtering the solution, and evaporating to the crystallizing point. (Kopp.) The salt belongs to the oblique prismatic system of crystallization, *Fig.* 118, but without any distinct plane of cleavage; $i : t = 107° 43'$; $u : u^1 = 80° 4'$; $u : t = 130° 8'$; $i : u = 101° 16'$; $i : a = 133° 20'$; $i : h = 100° 20'$. (Brooke, *Ann. Phil.* 22, 287.) It is isomorphous with sulphate of soda. Lemon-yellow; transparent; has an alkaline reaction and rough metallic taste. (John, Moser.) The crystals effloresce very rapidly (Brooke); they are permanent in the air, and become somewhat moist in a damp atmosphere only. (Moser.) They melt even with the heat of the hand; become opaque in alcohol from loss of their water of crystallization, and deliquesce rapidly in the air. (Kopp, *Ann. Pharm.* 42, 99.) They dissolve readily in water and sparingly in alcohol. (John, Moser.) An aqueous solution evaporated at a temperature above 30°, deposits the salt in the anhydrous state. (Kopp.)

	Crystallized.			Kopp.
NaO	31·2	....	18·01	46·45
CrO^3	52·0	....	30·02	
$10HO$	90·0	....	51·97	53·55
$NaO,CrO^3+10Aq.$	173·2	....	100·00	100·00

b. Bichromate.—Crystallizes in thin, hyacinth-red, six-sided prisms, bevilled at the extremities; it is more soluble than *a*, and consequently crystallizes out after it. (Moser.)

When a salt of chromic oxide is supersaturated with monocarbonate or bicarbonate of soda, the precipitated carbonate of chromic oxide is perfectly insoluble in excess of the re-agent.

C. Chromic oxide dissolves slowly in *borax*, and imparts to it in the inner blowpipe flame, an emerald-green colour, which increases in brilliancy on cooling; in the outer flame on platinum, the green colour is almost entirely converted into yellowish-brown, so that a mere tinge of the original colour is observable on cooling. (Berzelius.)

D. Chromic oxide dissolves in *microcosmic salt*, yielding a green glass, both in the inner and outer blowpipe flame. If an excess of the sesquioxide is added, the glass swells up every time it is cooled after ignition, and presents a frothy appearance, arising from an evolution of gas not yet explained; this takes place whether the fusion is effected in the outer or in the inner flame, on platinum or on charcoal. (Berzelius.)

E. SULPHATE OF CHROMIC OXIDE AND SODA.—*Soda-chrome-alum.*—A mixture of 2 parts (1 atom) of bichromate of soda and 3 parts (4 atoms) of oil of vitriol treated gradually with alcohol, so that its temperature may not rise too high, evolves aldehyde with violent effervescence, and deposits the alum, after long standing, in rounded masses, consisting of $NaO, SO^3+Cr^2O^3, 3SO^3+24Aq.$ This salt cannot be obtained in distinct crystals. At a temperature of 100°, the mass loses 16 atoms of water. It effloresces in the air more rapidly than ammonia or potash-chrome-alum, and its solution possesses the same characters as the solutions of these salts. (Schrötter.)

F. CHROMATE OF CHLORIDE OF SODIUM.—Deliquescent. (Pelouze.)

G. SESQUIFLUORIDE OF CHROMIUM + FLUORIDE OF SODIUM.—Green powder, very sparingly soluble in water. (Berzelius.)

H. CHROMATE OF SODA AND POTASH.—When the white porcelain-like mass obtained by fusing together 2 parts of bichromate of potash and 1 part of carbonate of soda, is dissolved in boiling water, it emits light on cooling (I. 208.), and deposits yellow crystals which have the form of sulphate of potash, and, like the latter, decrepitate when heated. The salt contains 36·39 per cent. of potash, 8·40 of soda, and 54·40 of chromic acid, $2(KO, CrO^3) + NaO, CrO^3$. (H. Rose, *Pogg.* 52, 585.)

I. SULPHOCHROMATE OF SODA AND POTASH.—Monochromate of potash and monosulphate of soda fused together in equivalent proportions, yield, when rapidly cooled, a fissured friable mass, which, on cooling from a boiling solution in water, is deposited, with vivid phosphorescence, in yellow crystals having the form of sulphate of potash; they decrepitate in the fire. These crystals are composed of 41·92 per cent. of potash, 9·21 of soda, 3·11 of chromic acid, and 45·62 of sulphuric acid. (H. Rose.)

Chromium and Lithium.

Chromate of Lithia.—Crystallizes in orange-yellow, oblique rhombic prisms, or in dendritic masses. It is readily soluble in water. (C. G. Gmelin.)

Chromium and Barium.

Chromate of Baryta.—Prepared by precipitating chromate of potash with chloride of barium or baryta-water. Baryta-salts are precipitated by chromate of potash at the same degree of dilution as by the sulphate. (J. D. Smith, *Phil. Mag. J.* 8, 260.) This compound forms a lemon-yellow powder, the colour of which, according to Moser, is rendered darker by prolonged ignition. It is not decomposed by cold sulphuric acid, and with difficulty by the same acid when hot. Aqueous solutions of the alkaline sulphates also do not affect it, even with the aid of heat, or but slightly. (Fischer, *Kastn. Arch.* 9, 356.) It is insoluble in water, but dissolves easily in nitric acid, hydrochloric acid, or excess of chromic acid, forming a reddish-yellow solution of bichromate of baryta; from this solution it is again precipitated by ammonia.

	Calculation.		Berzelius.	Vauquelin.
BaO	76·6	59·57	59·85	57·75
CrO^3	52·0	40·43	40·15	42·25
BaO,CrO^3	128·6	100·00	100·00	100·00

Chromium and Strontium.

Chromate of Strontia.—Formed by precipitating chromate of potash with chloride of strontium. Dilute solutions yield no precipitate. (J. D. Smith). Strontia-water does not affect chromate of potash. (Döbereiner.) Chromate of strontia is a pale yellow powder, very slightly soluble in water, but readily soluble in hydrochloric, nitric, and chromic acids.

Chromium and Calcium.

A. Chromate of Lime.—Monochromate of potash gives with chloride of calcium, a pale yellow precipitate which slowly subsides. (Thomson, Moser.) Carbonate of lime decomposes chromate of potash but partially, forming chromate of lime. (Kuhlmann, *Ann. Pharm.* 41, 229.) Lime-water does not precipitate chromate of potash. The yellowish-brown silky scales, very soluble in water, which Vauquelin obtained by dissolving lime in aqueous chromic acid, are regarded by Moser as an acid salt.

B. Chromate of Chloride of Calcium.—$CaCl, 2CrO^3$.—Deliquescent. (Pelouze.)

¶ C. Chromate of Lime and Potash. — $KO, CrO^3 + CaO, CrO^3 + 2HO$.—Prepared by saturating a solution of bichromate of potash with hydrate of lime, and passing carbonic acid through the clear liquid, evaporated at a temperature between 30° and 40°. When ignited it fuses, without decomposition. (Schweitzer, *J. pr. Chem.* 39,269.) ¶

Chromium and Magnesium.

¶ A. Chromite of Magnesia.—Obtained, mixed with magnesia, by decomposing the double chromate of magnesia and potash at a low red heat. The magnesia may be afterwards removed by a dilute acid. It has a fine brown colour, and is insoluble in acids and alkalis; its formula is MgO, Cr^2O^3. (Schweitzer.) ¶

B. Chromate of Magnesia.—Prepared by dissolving magnesia in chromic acid. Crystallizes in large transparent, orange-yellow, six-sided prisms, which dissolve readily in water. (Vauquelin.) The crystals are lemon yellow, and have the same form as those of sulphate of magnesia; at 15°, their specific gravity is 1·66. (Kopp.)

	Anhydrous.			*Crystallized.*		Kopp.
MgO	20	27·78	MgO	20	14·81	52·85
CrO^3	52	72·22	CrO^3	52	38·52	
			$7HO$	63	46·67	47·15
MgO, CrO^3	72	100·00	$+ 7Aq.$	135	100·00	100·00

C. Chromate of Chloride of Magnesium.—$MgCl, 2CrO^3$.—Deliquescent. (Pelouze.)

¶ D. Chromate of Magnesia and Potash.—$KO, CrO^3 + MgO, CrO^3 + 2HO$.—A moderately concentrated solution of bichromate of potash is digested with magnesia alba, and the clear liquid evaporated to the crystallizing point. Beautiful yellow crystals belonging to the oblique prismatic system, and resembling those of gypsum. When heated it becomes orange yellow, and fuses at incipient redness, evolving oxygen and leaving the compound A. (Anthon, *Buchner's Repert.* 34, 248, Schweitzer.) ¶

Chromium and Cerium.

Chromate of Cerous Oxide.—*a. Monochromate.*—Carbonate of cerous oxide dissolves freely in aqueous chromic acid; the solution is yellow, has a rough taste, and after some time deposits monochromate of cerous oxide, in the form of a yellow powder. (John.)—*b. Bichromate.*—The solution from which the normal salt is deposited, yields, on evaporation, small reddish crystals surrounded by an amorphous salt. (John.) The salt crystallizes in small, red, transparent prisms, soluble in water. (Berzelius.)

CHROMIUM AND YTTRIUM.

CHROMATE OF YTTRIA.—*a. Basic chromate.*—Aqueous chromic acid saturated with carbonate of yttria, forms a brown solution, which, after some time, deposits the basic salt in the form of a brown powder; on boiling the liquid, an additional quantity is thrown down, of a somewhat lighter colour, while monochromate of yttria remains in solution. (Berlin.)

b. Monochromate.—By evaporating the solution of carbonate of yttria in aqueous chromic acid, orange yellow dendritic crystals are obtained, which are neutral towards vegetable colours, of a rough and pungent taste, and readily soluble in water. (John.) The solution decanted from the salt *a*, yields by spontaneous evaporation, sometimes yellowish-brown, deliquescent, acicular crystals, and sometimes a brown amorphous residue. (Berlin.)

CHROMIUM AND GLUCINUM.

CHROMATE OF GLUCINA.—*a. Monochromate.*—A yellow salt insoluble in water.—*b. Acid chromate.*—The yellow solution yields a gummy uncrystallizable residue. (John, Berzelius.)

CHROMIUM AND ALUMINUM.

CHROMATE OF ALUMINA.—*a. Basic chromate.*—A solution of *b* mixed with monochromate of potash, converts the latter into bichromate, and deposits a basic salt, which, however, by long continued washing, is completely resolved into hydrate of alumina and the salt *b*, which dissolves. (Maus.)

b. Acid chromate.—By saturating aqueous chromic acid with hydrate of alumina and evaporating the solution, a horny mass is obtained, which in its chemical relations, resembles the quadrochromate of ferric oxide, and probably, therefore, has a similar composition: $Al^2O^3, 4CrO^3$. (Maus, *Pogg.* 11, 81.)

CHROMIUM AND THORINUM.

CHROMATE OF THORINA.—Prepared by double decomposition: It forms a pale yellow flocculent precipitate, which dissolves in excess of chromic acid, yielding an acid salt. (Berzelius.)

CHROMIUM AND SILICIUM.

A. *Chromate of Silica?*—According to Godon, when an aqueous solution of chromic acid is evaporated with hydrate of silica, a reddish-yellow insoluble powder is formed, which sustains the heat of a pottery furnace without decomposition. According to Quesneville, (*J. Pharm.* 16, 131; also *N. Tr.* 22, 1, 254), chromic acid dissolves a small quantity of hydrated silica, and again deposits it on evaporation; the precipitated silica may be freed from every trace of chromic acid by washing.

B. FLUORIDE OF SILICIUM AND CHROMIUM, and *Hydrofluate of Silica and Chromic Oxide.*—A solution of chromic oxide in hydrofluosilicic acid yields on evaporation, a transparent green, amorphous mass which deliquesces in the air, and, when it contains an excess of acid, swells up in the fire like alum, and again deliquesces if afterwards exposed to the air. (Berzelius, *Pogg.* 1, 201.)

C. Chromate of potash fuses with glass, and forms a transparent, emerald-green glass. Chromic oxide does not dissolve in glass, but merely renders it turbid. (Nasse.)

CHROMIUM AND TUNGSTEN.

TUNGSTATE OF CHROMIC OXIDE.—Green precipitate.
A solution of sulphotungstate of potassium gives with a chromic salt, a scanty greenish-brown precipitate; hence the compound of tersulphide of tungsten with sesquisulphide of chromium dissolves in water with tolerable facility. (Berzelius.)

CHROMIUM AND MOLYBDENUM.

Chromate of potash added to a solution of protochloride of molybdenum, precipitates basic chromate of molybdic oxide, sesquichloride of chromium remaining dissolved in the liquid. (Berzelius.)

A. CHROMATE OF MOLYBDIC OXIDE.—*a. Basic chromate.*—Precipitated from *b* or *c*, by the addition of ammonia, in greyish-yellow flakes, insoluble in water.—*b. Bichromate.*—The pale yellow aqueous solution yields by spontaneous evaporation, white or light yellow crystalline scales, or efflorescent needles; the salt when perfectly dry is white.—*c. Acid chromate.*—The brown aqueous solution dries up to a brown uncrystallizable mass, which has an effloresced, saline appearance, and redissolves in water without alteration. (Berzelius.)

B. CHROMATE OF MOLYBDIC ACID.—Aqueous chromic acid dissolves molybdic acid at a boiling heat, forming a yellow solution, which if the molybdic acid is in excess, solidifies to a yellow transparent jelly. The filtered solution yields on evaporation, a transparent, yellowish-brown, uncrystallizable varnish. Water resolves the latter into a brown substance which immediately dissolves, and a pale yellow powder likewise soluble in a larger quantity of water. (Berzelius, *Pogg.* 6, 384.)

C. MOLYBDATE OF CHROMIC OXIDE.—Molybdate of ammonia gives with sesquichloride of chromium, an apple-green precipitate (Moser), soluble in excess of the molybdate of ammonia. (Berzelius.)

D. SULPHOMOLYBDATE OF CHROMIUM.—$Cr^2S^3, 3MoS^3$.—Sulphomolybdate of potassium gives with chromic salts a dark brown precipitate, which assumes a greenish tinge after drying.

E. PERSULPHOMOLYBDATE OF CHROMIUM.—$Cr^2S^3, 3MoS^4$.—Persulphomolybdate of potassium gives a dark red precipitate with salts of chromic oxide. (Berzelius.)

CHROMIUM AND VANADIUM.

CHROMATE OF VANADIC OXIDE.—The brownish-yellow solution of hydrated vanadic oxide in aqueous chromic acid leaves when evaporated, a brilliant dark brown varnish, which dissolves but partially in water, forming a yellow solution, from which sulphuretted hydrogen throws down a pale green precipitate. (Berzelius.)

Other Combinations. With iron.

CHAPTER XXII.

URANIUM.

Klaproth. *Beiträge*, 2, 197; also *Crell. Ann.* 1789, 2,387.
Richter. Regulus of Uranium. *N. Gegenst. d. Chem.* 1, 1; 9, 36.—Uranic Oxide. *A. Gehl.* 4, 402.
Bucholz. *Beiträge*, 1, 62; *A. Gehl.* 4, 17 & 134.
Lecanu et Serbat. *J. Pharm.* 9, 141; also *Schw.* 44, 35.
Laugier. *J. Pharm.* 9, 145; also *Schw.* 44, 40.
Lecanu. *J. Pharm.* 11, 279.
Laugier & Boudet. *J. Pharm.* 11, 286.
Arfvedson. *Pogg.* 1, 245; also *Schw.* 44, 8.
Berzelius. *Pogg.* 1, 359; also *Schw.* 44, 191.—*Jahresber.* 22, 116.
Brande. *Quart. J. of Sc.* 14, 86; also *Schw.* 44, 1.
Peligot. *Compt. rend.* 1841, 735; also *J. pr. Chem.* 23, 494.—*J. Pharm.* 27, 525; also *Ann. Pharm.* 41, 141; also *J. pr. Chem.* 24, 442.—*N. Ann. Chim. Phys.* 5, 5; also *Ann. Pharm.* 43, 255; also *N. Ann. Chim. Phys.* 12, 258.
Ebelmen. *N. Ann. Chim. Phys.* 5, 189; also *Ann. Pharm.* 43, 286; also *J. pr. Chem.* 27, 385.
Rammelsberg. *Pogg.* 55, 318; 56, 125; 59, 1.
Wertheim. *J. pr. Chem.* 29, 209.
Werther. *J. pr. Chem.* 43, 321; abstr. *Ann. Pharm.* 68, 312; also *Pharm. Centr.* 1848, 433; also *Liebig & Kopp's Jahresb.* 1847—8, 419.

SYNONYMES; *Uran, Urane.*

History. Klaproth, in the year 1789, discovered in Pitchblende and Uranite a metallic oxide, to the metal of which he gave the name of uranium. Till lately, the protoxide (UO) obtained by exposing the green oxide ($U^3 O^4$) to a white heat in contact with charcoal, and also by other methods, was regarded as the real metal, and the atomic weight of uranium determined accordingly. But in 1841, Peligot discovered the error of this view, and accordingly the atomic weight of uranium was reduced to less than one-third its former amount. Peligot likewise prepared the pure metal.

Sources. In small quantities, as impure uranoso-uranic oxide (*Pitchblende*); as hydrated oxide (*Uranic ochre*); as sulphate of uranous oxide; as basic sulphate of uranic oxide; as phosphate of uranic oxide and lime; and as phosphate of uranic oxide and cupric oxide (*Uranite*); as tantalate of uranous oxide (*Uranotantalite*), (G. Rose, *Pogg.* 48, 555); and in small quantity in Yttrotantalite, especially in the yellow varieties, and in Euxenite.

Preparation. 1. A mixture—not exceeding 10 grammes—of one part of potassium and 2 parts of protochloride of uranium is introduced as rapidly as possible (to avoid the attraction of atmospheric moisture) into a small platinum crucible—the cover fastened down by a wire—and the whole heated over a spirit-lamp. Decomposition then takes place, the crucible becoming red-hot, and a portion of the mass being projected from it by the violence of the action. To prevent injury from the burning potassium, it is advisable therefore, before applying the heat, to enclose the crucible in a larger vessel of the same kind. After the action has ceased, the crucible is again placed over the lamp, and strongly heated to volatilize the remaining potassium, and also to fuse the chloride of patassium produced, and thereby facilitate the aggregation of the uranium. The contents of the crucible, when cool, are treated with cold water. —whereupon, hydrogen gas is evolved, either by the action of a small residual quantity of potassium, or—if the potassium has acted but imperfectly—by the action of ¾-chloride of uranium. The metal is washed with pure water. (Peligot.)—2. A solution of uranite of ammonia in hydrochloric acid is mixed with an excess of sal-ammoniac and about its own weight of common salt; the mixture evaporated to dryness; and the residue ignited in a covered crucible, till the sal-ammoniac is volatilized and the chloride of sodium fused, whereby access of air is prevented. The mass, after cooling, is digested in cold water, which removes the common salt and leaves metallic uranium*. (Wöhler, *Ann. Pharm.* 41, 345.)—Clarke obtained from pitchblende and from cupreous uranite, before the oxy-hydrogen blowpipe, a steel-grey metal, scarcely yielding to the hardest file, and not possessed of magnetic properties.

Properties. Sometimes in the form of a black powder, sometimes welded together on the sides of the crucible in silvery laminæ and fibrous masses, which yield to the file and appear to be somewhat ductile. (Peligot.)

¶ According to Berzelius, uranium exists in two allotropic states (corresponding to silicium, &c.). U*α* is prepared from the chloride by means of potassium, and is one of the most combustible bodies known; it likewise dissolves readily in dilute acids, with evolution of hydrogen. U*β*, obtained, according to Richter's method, by reducing uranic oxide with dried ox-blood at a high temperature, is not acted on by hydrochloric acid, though it dissolves in aqua-regia; these modifications may be traced in the soluble and insoluble forms of uranous oxide (p. 161).

* This process yields the protoxide, not the metal.

Atomic weight of Uranium. 59·43 (Ebelmen),—59·71 (Wertheim), —60 (Peligot, Rammelsberg),—64·2 (Berzelius),—59·7 (Werther).

Compounds of Uranium.

URANIUM AND OXYGEN.

The metal remains unaltered in the air at ordinary temperatures; when slightly heated, it takes fire and burns with a brilliant white light, increasing in bulk and being converted into uranoso-uranic oxide.—When heated on paper, it inflames before the latter takes fire; when thrown into the flame of a candle, it burns with brilliant scintillations. It does not decompose cold water, but dissolves in dilute acids, liberating hydrogen gas and forming a solution of uranous oxide. (Peligot.)

A. SUBOXIDE OF URANIUM? U^4O^3.

When an aqueous solution of three-fourths chloride of uranium is treated with ammonia, a brown precipitate is obtained, which is probably [the hydrate of] U^4O^3; the precipitate is converted in a few moments, with evolution of hydrogen gas, into a greenish yellow [hydrated] suboxide, containing a larger proportion of oxygen. The latter by exposure to the air, is first converted into brown hydrated uranous oxide, and then into yellow uranic oxide or uranate of ammonia. (Peligot.)

B. URANOUS OXIDE. UO.

Protoxide of Uranium, Uranoxydul.

Formerly mistaken for metallic uranium.

Preparation. 1. By exposing uranoso-uranic oxide mixed with $\frac{1}{20}$ of its weight of charcoal powder to the strongest heat of a blast-furnace. (Bucholz.)—Richter used bullock's blood, Klaproth used oil as the deoxidizing agent.—2. By igniting oxalate of uranic oxide alone and out of contact of air. (Berzelius.)—According to Peligot, the protoxide is obtained in the state of greatest purity by heating oxalate of uranic oxide to redness in a hard glass tube, in a current of hydrogen gas; the action is so violent that the current of hydrogen must be checked for a while, as otherwise the mass will be projected from the tube. The black oxide, U^4O^5, is first formed, and then the brown protoxide, UO. After the reduction is finished, the tube, still containing hydrogen, is sealed at both ends.—The protoxide thus obtained is mixed with charcoal, and, when dissolved in nitric acid, leaves blackish brown flakes. (Rammelsberg.)—3. Hydrogen gas, dried by passing over chloride of calcium, is conducted over finely divided and previously ignited uranoso-uranic oxide, heated to redness in a tube of glass or porcelain; the reduction is accomplished in a few minutes, the mass becoming red hot. (Arfvedson, Lecanu.)—If the uranoso-uranic oxide is dense—as, for instance, when it is obtained by igniting the nitrate of uranic oxide—it must be frequently agitated in the tube during the above process, in order to ensure its complete reduction to the state of protoxide. (Rammelsberg).—4. By passing hydrogen gas in the same manner over red-hot chloride of uranous oxide and potassium —whereby hydrochloric acid is produced—and removing the chloride of potassium and undecomposed salt by digestion in water. (Arfvedson.)—The same result may be obtained by simply igniting the double chloride of uranous oxide and potassium, or—what is the same thing—the residue obtained by evaporating to dryness the solution of uranate of potash in hydrochloric acid. (Peligot.)

Properties. As prepared by the first method, this oxide is iron-grey and earthy; and, when examined by the microscope, appears to be composed of small needles, having a faint metallic lustre. (Bucholz.) Specific gravity = 6·44 (Klaproth); 6·94 (Richter); 9·0 (Bucholz).—Very refractory (Bucholz.) When prepared by the second method, it forms a cinnamon-brown powder (Peligot),—a copper-red, crystalline powder with metallic lustre, and of specific gravity 10·15. (Ebelmen.) The powder, when oxidized in the air, and again reduced by hydrogen gas, appears dark-red, and destitute of metallic lustre. (Ebelmen.)—When prepared by the third method, it is a liver-coloured powder (Arfvedson); a black powder (Laugier, Boudet).—The fourth method yields it in the form of a metallic-shining powder, which, under the microscope, appears to consist chiefly of regular octohedrons, having a strong metallic lustre; at the edges, however, they are slightly translucent, transmitting light of a reddish-brown colour; they yield a reddish-brown powder. (Arfvedson.)—Crystalline scales, having the metallic lustre. (Peligot.)

Calculation, according to Peligot.

U	60	....	88·24
O	8	....	11·76
UO	68	....	100·00

(UO = 802·49 + 100 = 902·49. Berzelius.)

That this oxide is not metallic uranium, is proved by the following facts:—When it is mixed with lamp-black, and strongly ignited in a current of hydrogen gas till no more water is produced, the residue does not contain metallic uranium, but the protoxide; for on passing chlorine over it, carbonic acid and carbonic oxide are formed, together with a sublimate of protochloride of uranium. When protoxide of uranium, prepared by the fourth method is ignited in chlorine gas, it likewise yields chloride of uranium, carbonic acid and carbonic oxide. (Peligot.)—Potassium, at the temperature at which it sublimes, does not abstract oxygen from uranous oxide. (Plantamour, *J. pr. Chem.* 23, 230.)—Hydrochloric acid gas, passed over ignited uranous oxide, produces no change in it, beyond destroying its tendency to take fire in the air at ordinary temperatures. (Peligot.)—Peligot regards uranous oxide, in some of its combinations, as a compound metal $U^2 O^2$, which, though it contains oxygen, nevertheless plays the part of a simple metal. To distinguish this compound from pure uranium, Peligot calls it *Uran* or *Uranyl.* But though many uranium compounds exhibit peculiarities which seem to favour this view (vid. *Salts of Uranic oxide, Chloride of Uranous oxide,* and *Chloride of Uranous oxide and Potassium*), there is at present no absolute necessity for adopting it. [For objections to this theory, see Berzelius, *Jahresb.* 1843, 114, and Kühn, *Ann. Pharm.* 41, 337. On the contrary: Peligot, *N. Ann. Chim. Phys.* 12, 549.]

Combinations.—*a.* With Water. HYDRATE OF URANOUS OXIDE. Ammonia, potash, or soda, added to a salt of uranous oxide—the hydrochlorate, for example—throws down reddish brown, gelatinous flakes, which, on boiling the liquid, turn black and increase in density, probably from loss of water. The precipitate, when freed from every trace of ammonia, remains brown even if exposed to the air; but, if it be merely washed with cold water, it still retains ammonia, and, on exposure to the air, is converted into yellow uranate of ammonia. (Peligot.)

b. With Acids, forming the SALTS OF URANOUS OXIDE, or URANOUS SALTS.—Uranous oxide, when obtained by ignition, is insoluble in boiling dilute hydrochloric or sulphuric acid, but dissolves in strong oil of vitriol. The hydrate is easily soluble in acids. The green solution, when evaporated, yields green or greenish white salts. Uranous salts in solution are converted into uranic salts: by exposure to the air, by the action of nitric acid even at ordinary temperatures, and by gold or silver salts, the action in this case being accompanied by precipitation of metallic gold or silver. The alkalis, and even carbonate of lime, precipitate from these salts a reddish brown, gelatinous hydrate of uranous oxide. Alkaline carbonates, added to solutions of uranous salts, give off carbonic acid, and throw down a green precipitate, which, when washed and dried, consists of pure hydrated uranous oxide. This precipitate is soluble in excess of the reagent, especially in carbonate of ammonia, and forms a green solution. (Rammelsberg.)

C. BLACK URANOSO-URANIC OXIDE. U^4O^5.

The residue obtained by strongly igniting green uranoso-uranic oxide or nitrate of uranic oxide. To prevent it reabsorbing oxygen as it cools, and passing again to the state of green oxide, the red-hot crucible must be closely covered and placed upon a thick metallic plate, so that it may cool rapidly. When this oxide is ignited in a current of hydrogen gas, it gives up 3 per cent. of oxygen, and is reduced to the state of uranous oxide. [$U^4O^5—O=4UO$; $280 : 8=100 : 2·86$.] It dissolves in acids, forming a mixture of uranous and uranic salts. (Peligot.) Ebelmen regards this oxide as a mere mixture of UO and U^3O^4.—According to Rammelsberg's experiments also (*Pogg.* 59, 5), the existence of a distinct black uranoso-uranic oxide is a matter of doubt. The uranoso-uranic oxide obtained by strongly igniting nitrate of uranic oxide, increased in weight by gentle ignition in the air, sometimes to the amount of 0·04 per cent. only, and sometimes not at all; uranic oxide, after gentle ignition in the air, was reduced in weight by only 0·09 per cent. when strongly heated in a wind-furnace. [Probably the carbonic oxide disengaged in the furnace exerts a slight deoxidizing action.]

Calculation, according to Peligot.			Or:		
4U	240	85·71	2UO	136	48·57
5O	40	14·29	U^2O^3	144	51·43
U^4O^5	280	100·00	$2UO,U^2O^3$	280	100·00

D. GREEN URANOSO-URANIC OXIDE. U^3O^4.

Formerly regarded as the *Protoxide.*—Occurs in an impure state, as *Pitchblende.*—*Formation.*—1. By burning the metal (p. 158).—2. By burning the protoxide.—The protoxide prepared by the second method (p. 159) takes fire in the air at ordinary temperatures, and is converted, with continuous but feeble glow, into the black oxide; and this, when heated for a longer time, turns green. (Peligot.) This pyrophoric property of uranic oxalate after being heated in a current of hydrogen gas, appears to be due to condensed hydrogen; for, on burning the protoxide thus obtained in a current of oxygen, a small quantity of water is invariably produced. (Rammelsberg.) The protoxide prepared by the second method, when kept for a long time at a temperature between 150° and 200°, turns black (without emission of light or heat), and then, after complete saturation with oxygen, assumes, in the course of 12 or 15 hours, a green colour. (Ebelmen.) The more coherent variety of uranous oxide obtained by the first, third, or fifth method (p. 159), does not take fire till it is heated to incipient redness: it then burns with intumescence like a coal, and is converted into uranoso-uranic oxide. (Bucholz, Arfvedson, Peligot.) Under these circumstances, 100 parts of uranous oxide absorb from 3·695 to 3·73 parts of oxygen, according to Arfvedson; 3·9 parts, according to Ebelmen; and 40 parts, according to Peligot.

$$3UO + O = U^3O^4; \quad 204 : 8 = 100 : 3{\cdot}92.$$

In the flame of the oxy-hydrogen blowpipe, uranous oxide burns with scintillation. (Clarke.)—3. By gentle ignition of the sesquioxide.—The green oxide is almost invariably formed, when any other oxide, or the metal itself, is exposed to the air for some time in a state of gentle ignition; at a higher temperature, on the contrary, the black oxide is produced. (Peligot.)—4. Uranous oxide, heated to redness in an atmosphere of aqueous vapour, decomposes it slowly, with formation of uranoso-uranic oxide. (Regnault, *Ann. Chim. Phys.* 62, 358.)

Preparation.—From *Pitchblende,* which, besides 40....95 per cent. of uranoso-uranic oxide, may also contain sulphur, selenium, phosphoric acid, lime, magnesia, alumina, silica, vanadium, manganese, arsenic, bismuth, antimony, zinc, tin, lead, iron, cobalt, nickel, copper, and silver.—1. Powdered pitchblende is dissolved in warm nitro-hydrochloric acid, and after all action has ceased, the excess of acid is expelled by evaporation; the residue treated with a small quantity of hydrochloric acid; water added; and the solution filtered from sulphur and silica (and also from chloride of lead and silver: *Wittstein*). The arsenic, lead, and copper (with bismuth and tin: *Wittstein*), are then precipitated from the filtrate by sulphuretted hydrogen, and the solution again filtered and boiled, nitric acid being added to convert the protoxide of iron into sesquioxide. The liquid is then supersaturated with a large quantity of carbonate of ammonia, which throws down the oxide of iron, together with any lime that may be present, and the greater part of the cobalt and zinc oxides, retaining in solution the uranic oxide, together with portions of the cobalt and zinc oxides. [The filtrate often deposits carbonate of lime in crystals.] The filtrate is boiled as long as carbonate of ammonia continues to be evolved, by which means the three metallic oxides are precipitated, with the exception of a small quantity of cobalt oxide, which colours the liquid red; the precipitate is collected on a filter, and afterwards washed, dried, and ignited, till its yellow colour changes to blackish green. The resulting mixture of uranoso-uranic oxide, uranate of zinc, and uranate of cobalt, is lastly digested for several hours with cold dilute hydrochloric acid, which dissolves the two compounds of uranic oxide, and leaves pure uranoso-uranic oxide undissolved. (Arfvedson.) Wittstein (*Repert.* 63, 231), after boiling the solution with nitric acid, precipitates with caustic ammonia, instead of carbonate of ammonia (thereby retaining the lime, magnesia, and zinc in solution); washes the precipitate by decantation, out of contact of air; heats it in a close vessel with water and a quantity of carbonate of ammonia equal in weight to half the pitchblende used; filters hot; treats the residue once more with carbonate of ammonia; evaporates the filtrate to dryness; completes the operation by heating the residue, and thus obtains uranic oxide, contaminated however with oxide of iron. Persoz (*Ann. Chim. Phys.* 58, 202) treats the solution with nitric acid, and then boils it with oxide of copper or of lead, which precipitates the uranic and ferric oxides; dissolves the washed precipitate in nitric acid; boils the solution with mercuric oxide, which throws down nothing but ferric oxide; dilutes the filtrate with water; and removes the mercury and copper by a current of sulphuretted hydrogen. The solution after this treatment retains nothing but uranium.

2. The finely divided pitchblende is freed by elutriation from the lighter earthy impurities; roasted for a short time to save nitric acid; then dissolved in that acid, and the solution evaporated to dryness. The residue is exhausted with water; the solution filtered from the brick-red mixture of ferric oxide, arseniate of ferric oxide, and sulphate of lead; the greenish-yellow filtrate slightly evaporated, and allowed to cool, whereupon it deposits crystals; and the resulting radiated mass of crystallized nitrate of uranic oxide, drained on a glass funnel, and then washed with a small quantity of cold water. As the water dissolves a portion of the uranium salt, it is used in a subsequent operation to redissolve the dry residue obtained by evaporating the solution of pitchblende in nitric acid. The uranic nitrate after being dried in the air, is then introduced into a wide-mouthed bottle containing ether, in which it immediately dissolves; the yellow solution is left to evaporate spontaneously in the air, and the crystals obtained are purified by solution in hot water and recrystallization. They are converted into uranoso-uranic oxide by ignition. From the mixed mother-liquids diluted with water, arsenic, lead, and copper are precipitated by sulphuretted hydrogen, and ferric oxide removed from the filtrate by evaporating to dryness, and redissolving in water. The solution thus obtained yields a fresh crop of crystals of uranic nitrate. (Peligot.)

3. Ebelmen frees the pitchblende, by digestion in dilute hydrochloric acid, from the adhering carbonates of lime, magnesia, protoxide of manganese, and oxide of copper; then washes it with boiling water; mixes it with charcoal; ignites strongly, whereby a portion of the sulphur and arsenic is expelled; treats the cooled mass with strong hydrochloric acid, which dissolves lead, iron, and a small quantity of copper (without any uranium); washes the residue with a large quantity of water; and roasts it to expel the remaining sulphur and a portion of the arsenic. After this, he treats the mass with nitric acid, which leaves quartz-sand and ferric oxide undissolved; evaporates the solution containing alumina, uranium, arsenic, lead, iron, copper, and even antimony, nearly to dryness; redissolves the residue in boiling water, which leaves the greater part of the iron and arsenic in the form of insoluble arseniate of ferric oxide; boils the filtrate with sulphurous acid; precipitates the rest of the arsenic, together with the copper and lead [and antimony], by a current of hydrosulphuric acid; evaporates the filtrate, which now contains nothing

but uranic oxide with a small quantity of ferric oxide and alumina, to dryness; dissolves in water, which leaves the ferric oxide; and purifies the uranic nitrate by repeated crystallization. From the mother-liquids obtained in this process, the ferric oxide and alumina are precipitated by careful addition of a small quantity of ammonia; and the filtrate mixed with excess of ammonia to precipitate the uranic oxide, which—after being ignited and freed from any adhering lime, magnesia, and protoxide of manganese, by cold, moderately strong, hydrochloric acid—is washed, dissolved in nitric acid, and obtained in the crystallized state as nitrate of uranic oxide. If the crystallized uranic nitrate is required absolutely pure, it must be dissolved in a small quantity of water; a hot concentrated solution of oxalic acid added to the liquid; and the precipitated uranic oxalate washed with boiling water, and converted into uranous oxide by ignition in a covered platinum crucible. The uranous oxide is then to be digested for some time in concentrated hydrochloric acid; washed with water; dissolved in nitric acid; crystals of uranic nitrate obtained from the solution; the crystals redissolved in water, and again precipitated as above by oxalic acid; the precipitate again washed with hot water, and lastly ignited in the air. (Ebelmen.)—Pitchblende (*Pechuran*) is dissolved in warm dilute nitric acid; the filtrate freed by hydrosulphuric acid from arsenic, lead, and copper, and then evaporated to dryness; the residue digested in water, which leaves the oxides of manganese, iron, and cobalt, undissolved; and the uranic nitrate contained in the solution, purified by repeated crystallization. (Wertheim, *J. pr. Chem.* 29, 210.)

4. An intimate mixture of pitchblende with half its weight of nitre* is kept at a red heat in a crucible for 20 minutes, and frequently stirred; the fused mass exhausted by repeated decantation with water, which dissolves the silicate of potash; and the insoluble portion treated with excess of pure concentrated nitric acid, which leaves the greater part of the ferric oxide undissolved. The clear liquid is poured off and evaporated nearly to dryness; the greenish residue mixed with water, which separates ferric oxide (from which the still adhering uranic oxide is separated as far as possible by solution in nitric acid); the solution filtered; again evaporated to dryness to decompose the remaining ferric nitrate; and redissolved in water, to which, if the uranic oxide does not entirely dissolve, a portion of nitric acid is added. Lastly the filtrate containing oxide of lead, uranic oxide, and lime is mixed with excess of carbonate of ammonia till the precipitate, which is yellow at first, becomes white; the solution is then filtered from carbonate of lime and oxide of lead, and lastly, boiled and evaporated to dryness, to separate the whole of the uranic oxide, which is then calcined. (Lecanu & Serbat.) It is better to evaporate to dryness, and treat the residue with water only. By this means the nitrate of ammonia is dissolved free from uranic oxide, while carbonate of uranic oxide remains undissolved. (Laugier.) Carbonate of ammonia is preferable to carbonate of potash or soda, because it does not dissolve the oxide of lead. (Lecanu & Serbat.) Quesneville (*J. Pharm.* 15, 494), who in other respects follows Arfvedson's method, uses sal-ammoniac mixed with carbonate of potash or soda, instead of the carbonate of ammonia, on account of the costliness of the latter; but the saving is probably but trifling.

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* Laugier states that from 1 to 1½ pt. nitre to 1 pt. pitchblende is required for the complete oxidation of the uranium.

5. To 8 parts of very finely powdered pitchblende contained in a capacious vessel, 9 or 10 parts of oil of vitriol are gradually added, the mixture being well stirred with an iron rod; whereupon the mass increases greatly in bulk, and becomes hard and lumpy. It is then kept in a warm place for several days and stirred frequently, during which time it absorbs water and becomes thinner and greyish white. It is then evaporated to dryness in an iron vessel; the mass broken up and again heated more strongly, with constant stirring, as long as the sulphuric acid in excess continues to evaporate, and till the residue assumes a dull reddish-yellow colour. When cold, it is repeatedly boiled with fresh quantities of water; and the greenish-yellow filtrate saturated with hydrosulphuric acid, of which a small quantity only is required, as the greater part of the metals precipitable by it are left behind in the insoluble residue. The solution is then filtered from the sulphides; the hydrosulphuric acid expelled by boiling; the liquid again filtered from any precipitate that may have formed; the filtrate boiled for some time with nitric acid, to convert the uranous oxide into uranic oxide; supersaturated after cooling with a dilute solution of carbonate of ammonia; set aside for some time, and frequently stirred; and lastly, filtered and boiled, till carbonate of uranic oxide separates from the liquid; the precipitate thus obtained is well washed with water. The filtrate yields sulphate of ammonia by evaporation. One part of powdered pitchblende may also be heated with 5 parts of bisulphate of soda (as obtained in the preparation of nitric acid from Chili-saltpetre), till the mixture fuses tranquilly; the greenish-yellow mass reduced to powder, and exhausted with boiling water; and the filtrate treated as above with hydrosulphuric acid, nitric acid, and carbonate of ammonia. (Werner, *J. pr. Chem.* 12, 381.) The methods of Richter and Bucholz are less satisfactory, that of Brande least of all.

Properties.—As obtained by burning the metal or by igniting the carbonate of uranic oxide, it forms a dull green powder. (Arfvedson.) Dark olive green, velvet-like powder. (Peligot.) That obtained by igniting uranate of ammonia forms black, very dense, hard fragments, which likewise yield a dingy green powder. (Arfvedson.) Sp. gr. = 7·1932 (Karsten.) = 7·31 (Ebelmen.)

Calculation, according to Peligot.			Or:		
3U	180	84·91	UO	68	32·08
4O	32	15·09	U^2O^3	144	67·92
U^3O^4	212	100·00	UO, U^2O^3	212	100·00

Or:			Peligot.	Marchand.	Arfvedson.
3UO	204	96·23	96·2	96·4	96·465
O	8	3·77	3·8	3·6	3·535
U^3O^4	212	100·00	100·0	100·0	100·000

	Berzelius.	Bucholz.	Schönberg.
3UO	96·44	95·1	94
O	3·56	4·9	6
U^3O^4	100·00	100·0	100

$U^3O^4 = 3 . 802·49 + 4 . 100 = 2807·47$. (Berzelius.)

Berzelius, Arfvedson, Peligot, Marchand (*J. pr. Chem.* 23, 498), and Rammelsberg, estimate the amount of oxygen by the loss of weight which the uranoso-uranic oxide sustains when converted into uranous oxide by ignition in hydrogen gas.

Peligot attributes the smaller loss of weight obtained by Arfvedson to the fact of his green oxide being mixed with a portion of black oxide. According to Rammelsberg, however, the loss varies between 3·83 and 4·67 per cent., and, accordingly, cannot serve for the exact determination of the atomic weight of uranium.

Decompositions.—1. By strong ignition, with loss of from 0·7 to 1 per cent. of oxygen, leaving black oxide. (Peligot.)—2. By potassium, sodium, charcoal, hydrogen, or sulphur at a red heat, it is converted into uranous oxide. The action of potassium on soda is attended with slight incandescence. (Gay-Lussac & Thénard.) Hydrogen gas acts rapidly, the oxide becoming red-hot. (Arfvedson.) By ignition with sulphur, uranoso-uranic oxide is converted into black uranous oxide entirely free from sulphur. (Ebelmen.)

Combinations.—*a.* With water.—HYDRATED URANOSO-URANIC OXIDE.—1. Formed when a solution of uranoso-uranic oxide in an acid is precipitated by ammonia.—2. When protochloride of uranium is precipitated by ammonia, the hydrated protoxide which separates, absorbs oxygen during the washing and is converted into hydrated uranoso-uranic oxide. (Rammelsberg.)—3. A solution of uranic oxalate, exposed to the direct rays of the sun, deposits a violet-brown flocculent precipitate of hydrated uranoso-uranic oxide, which must be collected before the whole of the salt is decomposed, so that it may not become contaminated with hydrated uranic oxide. It is washed with boiling water, and dried in vacuo on a heated support. (Ebelmen.)

The hydrate obtained by the first method is dark greyish green (Berzelius), or sometimes purple-brown. (Arfvedson.)—When heated for several hours in the solution, it condenses to a heavy powder. (Arfvedson.)—When prepared by the second method, it is greenish black. (Rammelsberg.)—The third method yields it in a solid black mass, with brilliant conchoidal fracture; when ignited in a current of nitrogen gas, it gives off its water without any change of appearance, and still yields a green powder. (Ebelmen.)

	Dried in vacuo over oil of vitriol.		Rammelsberg (2).
U^3O^4	212	88·70	89·06
3HO	27	11·30	10·94
$U^3O^4,3HO$	239	100·00	100·00

The hydrate loses its water when heated, and leaves green uranoso-uranic oxide. (Arfvedson.) An aqueous solution of carbonate of ammonia resolves it into uranic oxide, which dissolves an insoluble brown hydrate of uranous oxide. (Berzelius.) When the hydrate precipitated by the first or second method is exposed to the air in a moist state, it is converted—if any alkali still adheres to it—into a yellow uranate of the alkaline base. (Arfvedson.)

b. With Acids, forming the SALTS of URANOSO-URANIC OXIDE, or URANOSO-URANIC SALTS.—Uranoso-uranic oxide, after ignition, dissolves very slowly and sparingly in dilute hydrochloric and sulphuric acids; more readily, however, in the concentrated acids, and completely in boiling oil of vitriol. (Arfvedson.) The uranoso-uranic oxide obtained by burning the metal dissolves readily in acids. (Lecanu.) The hydrate dissolves very easily, excepting when its density has been increased by heating it for several hours in the liquid from which it was precipitated. (Arfvedson.) The yellowish green solution thus obtained may be supposed to consist of a mixture of uranous and uranic salts; hence, from a solution of the green oxide in sulphuric acid, alcohol precipitates sulphate of uranous oxide, whilst sulphate of uranic oxide remains dissolved, and imparts a pure yellow colour to the liquid. A concentrated solution of the green oxide in hydrochloric acid behaves in the same manner, on the addition of sulphuric acid and alcohol. (Berzelius.) The uranoso-uranic salts have a green colour and rough taste. By exposure to the air, and by the action of nitric acid, even in the cold, they are converted into uranic salts. They are precipitated greyish green, or brown, by pure alkalis. With alkaline carbonates they yield dingy, light green precipitates, soluble in excess of the precipitant and forming a greenish solution. With phosphate of soda they yield dull greenish white precipitates; black with alkaline hydrosulphates; pale yellowish green, with oxalic acid, even when that acid is in large excess; brownish red, with ferrocyanide of potassium; and, according to Berzelius, reddish brown with tincture of galls. Hydrosulphuric acid has no action on these salts.

E. URANIC OXIDE. U^2O^3.

Sesquioxide of Uranium, Uranoxyd.

Uranium and its lower oxides dissolve readily in nitric acid, with evolution of nitric oxide and formation of uranic nitrate. Uranous oxide decomposes nitrate of silver in solution, without evolution of gas, metallic silver being precipitated and uranic nitrate formed. (Ebelmen.) The hydrate of uranous or uranoso-uranic oxide is not converted into uranic oxide by exposure to air in a moist state, unless an alkali is present, with which the uranic oxide can combine. (Peligot.)

Preparation. 1. By heating the hydrate of uranic oxide to a temperature not exceeding 300°. (Ebelmen.) According to Malaguti, the residue still contains water [Vid. *Hydrate of Uranic Oxide*].—2. By keeping the double carbonate of uranous oxide and ammonia at a temperature of about 300° for a considerable time, till the whole of the ammonia and carbonic acid are expelled. (Ebelmen.)

	Calculation, according to Peligot.	
2U	120	83·33
3O	24	16·67
U^2O^3	144	100·00

Or:			Arfvedson.	Schönberg.
2UO	136	94·44	94·73	91·3
O	8	5·56	5·27	8·7
	144	100·00	100·00	100·0

($U^2O^3 = 2 \,.\, 802{\cdot}49 + 3 \,.\, 100 = 1904{\cdot}98$. Berzelius.)

Formerly, UO, or rather 3UO, was regarded as metallic uranium, U^3O^4 as the protoxide, or as containing one atom of oxygen, and U^2O^3 (as at present) as a combination of 2 atoms of uranium with 3 atoms of oxygen. These oxygen compounds are now expressed by the following formulæ: The former metal, now the protoxide = UO; the former protoxide, now uranoso-uranic oxide = U^3O^4; the sesquioxide = U^2O^3. If in each of these formulæ we suppose 3U to be present, and deduct U^3O^3, which represents the former metal, we obtain the following proportions of oxygen between the former protoxide and the sesquioxide.

	The former metal.	The former protoxide.	Sesquioxide.
	U^3O^3	U^3O^4	$UO^{4\frac{1}{2}}$
$-U^3O^3 =$	$^\circ$	O	$O^{1\frac{1}{2}}$

Hence it is apparent: first, why both in the former and in the present protoxide the proportion of oxygen to the former or present sesquioxide is $= 2 : 3$; and secondly, why the present atomic weight of the protoxide and sesquioxide of uranium should be a third of its former amount. According to Arfvedson and Berzelius, the atomic weight of uranium, formerly so called, was 217; this is now regarded as U^3O^3; and if from this we deduct the atomic weight of 3 atoms of O, the atomic weight of 3 atoms of U will be $= 193$; consequenlty that of one atom of $U = 64{\cdot}3$; but according to the researches of Peligot, Rammelsberg, Ebelmen, and Wertheim, the actual atomic weight is 60.

Decompositions. By simple ignition, into oxygen gas and green uranoso-uranic oxide. (Ebelmen.)

Combinations. *a.* With water.—HYDRATED URANIC OXIDE.—Occurs native in the form of *Uranium-ochre*, a lemon-yellow, friable substance, which, when ignited, gives off water and oxygen gas, and is converted into the green oxide. (Berzelius, *Pogg.* 1, 374.)—1. An aqueous solution of uranic oxalate is exposed to the direct rays of the sun, till the brown precipitate of hydrated uranoso-uranic oxide, which first appears, turns yellow, and all the oxalic acid is resolved into carbonic acid and carbonic oxide; the precipitate is then purified with water, and dried in the air. (Ebelmen.)—2. A solution of uranic nitrate in absolute alcohol is evaporated at a moderate heat, not reaching to the boiling point, till, at a certain degree of concentration, nitric ether is disengaged; from the residual orange-yellow spongy mass, the undecomposed uranic nitrate is dissolved by water, and the remaining hydrated oxide is then washed continuously with boiling water. (Malaguti, *Compt. rend.* 16, 851.)

Hydrated uranic oxide, when dried in the air, has a lemon-yellow colour; when dried in vacuo, it acquires a shade of orange-yellow. It is permanent in the air; does not absorb carbonic acid; exposed to a temperature of 300°, it yields anhydrous uranic oxide; at a red heat it is converted into green uranoso-uranic oxide. (Ebelmen.)—At 15° it exhibits a lemon-yellow colour, and has a specific gravity of 5·926. At 400° it loses only a third of its water; at a higher temperature, the whole is given off (if it be perfectly free from acid); a portion of oxygen gas, however, always escapes with the last traces of water, leaving a brown mixture of the olive-green and black oxides of uranium. (Malaguti.)

Calculation.

	a.		Ebelmen.	Malaguti.
U^2O^3	144	94·12	93·75	93·89
HO	9	5·88	6·25	6·11
U^2O^3,HO	153	100·00	100·00	100·00

	b.		Ebelmen.
U^2O^3	144	88·89	88·35
2HO	18	11·11	11·65
$U^2O^3,2HO$	162	100·00	100·00

a is the hydrate dried at ordinary temperatures in vacuo, or at 100° in the open air.—*b* is the hydrate dried in the air at ordinary temperatures.

b. With Acids, forming the SALTS OF URANIC OXIDE, or URANIC SALTS. These salts are obtained by oxidizing the uranous or uranoso-uranic salts by nitric acid or by exposure to the air, and in an impure state by dissolving the alkaline uranates in acids. Most of them contain one atom of U^2O^3 combined with one atom of acid. This fact, according to Peligot, tends to establish the assumption that 2UO or U^2O^2 is a compound metal (*Uranyl*), and that uranic oxide, U^2O^3, should rather be considered as the oxide of uranyl $(U^2O^2)+O$; for, other bases containing 3 atoms of oxygen, *e.g.* Al^2O^3, Cr^2O^3, Fe^2O^3, require, 3 atoms of acid to produce a normal salt. According to Berzelius, however, this oxide forms sulphates composed of $U^2O^3,2SO^3$ and $U^2O^3,3SO^3$, as well as U^2O^3,SO^3,—and a nitrate containing $U^2O^3,3NO^5$, as well as that which is composed of U^2O^3,NO^5: now, since nitric acid does not form acid salts, the latter must be regarded as the normal; and the former, as well as the other salts, which to one atom of base contain only one atom of acid, must be considered as basic salts, notwithstanding their solubility and acid reaction. (*Vid.* pp. 173 and 177.)

The uranic salts have a yellow colour; they are mostly soluble in water, and when dissolved, have a very rough taste, without any subsequent metallic flavour. Most of them redden litmus. The sulphate and nitrate of uranic oxide turn turmeric brown even when they contain excess of acid. (Bucholz.) Those which contain a volatile acid part with it at a red heat. They are reduced to uranous salts by hydrosulphuric acid (Berzelius); also by trithonic acid (Persoz); and by alcohol or ether in direct sunshine. (Bucholz.)—Hydrochlorate of uranic oxide, supersaturated with hydrochloric acid, is converted by metallic zinc, cadmium, tin, lead, iron, cobalt or copper (with formation of dichloride of copper), into hydrochlorate of uranous oxide; by the prolonged action of zinc, a green or brown viscid mass is produced, which appears to be a compound of oxide of zinc with protoxide of uranium; from a solution of monohydrochlorate or nitrate of uranic oxide, zinc separates only a small quantity of uranic oxide, which, by enveloping the zinc, prevents any further action. (Fischer, *Pogg.* 9, 265; 16, 126.) With pure ammonia, potash, or soda, these salts give an orange-yellow precipitate (alkaline uranate) insoluble in excess of the reagent;—with carbonate of ammonia, potash, or soda—pale yellow, soluble in an excess of the alkaline carbonate (less readily in monocarbonate than in bicarbonate of potash and sesquicarbonate of ammonia, which latter solution again yields a precipitate on boiling*); also with carbonate of lime (Fuchs);—with phosphate of soda —unless the acid in the uranium solution is in too large excess—yellowish white (phosphate of uranic oxide);—with alkaline hydrosulphates, brownish black (sulphide of uranium, which takes a long time to settle completely down to the bottom of the vessel, so that the liquid remains black for a considerable time);—with sulphite of ammonia on boiling, yellow granular sulphite of uranic oxide;—with oxalic acid and alkaline

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[*] ¶ Ebelmen states that 1 part of the salt dissolved in 333 parts of water gives a bright yellow colour with carbonate of potash, 1 part in 666 pts., a distinct yellow; 1 part in 2664 pts., a yellow colour, perceptible after some minutes, with pure potash; 1 part in 5328 pts., a faint yellow tinge; 1 part in 10,656 pts., a distinct opalescence, after half an hour. (*N. Ann. Chim. Phys.*, 5, 189.) ¶

oxalates, yellow (oxalate of uranic oxide)—with alkaline succinates, yellow, from a solution containing not less than one part in 1000;—with tincture of galls, chocolate-brown;—with ferrocyanide of potassium, bright brownish red. (Klaproth, Berzelius.)—Before the blowpipe with fluxes, the salts give the same characters as uranic oxide itself.—The salts of uranic oxide form with salts of the alkalis, a great number of yellow double salts, in which the former lose their acid on exposure to heat, but with less facility than when uncombined.

c. With electro-positive salifiable bases, producing compounds which may be called *Uranates.* The compounds of uranic oxide with all the alkalis are formed by precipitating a uranic salt with an alkali; the uranates of baryta, lime, magnesia, and various heavy metallic oxides, are formed by adding ammonia to a mixture of a uranic salt with one of these bases; in this case, however, the precipitate contains more or less uranate of ammonia. The uranates are for the most part yellow, and, after ignition, orange-yellow. The uranic oxide contained in them remains undecomposed at a red heat, provided the base is permanent in the fire; at a white heat, however, it is generally reduced to uranoso-uranic oxide. Hydrogen gas, at a red heat, reduces the uranic oxide to metal [protoxide], and generally also the other metallic oxide (the alkalis excepted); the residual mass, after ignition with hydrogen, is in all cases inflammable in the air at ordinary temperatures. (Arfvedson.)

URANIUM AND CARBON.

A. CARBONATE OF URANOSO-URANIC OXIDE.—Sulphate of uranoso-uranic oxide gives with carbonate of ammonia, not in excess, a pale green precipitate. (Arfvedson.)

B. CARBONATE OF URANIC OXIDE.—Remains in the form of a bright orange-yellow powder on gently heating the double carbonate of uranic oxide and ammonia. (Lecanu, Peligot.) [See also Ebelmen, p. 182.]—The lemon-yellow precipitate obtained on treating nitrate of uranic oxide with carbonate of potash, after being washed with cold water and dried in the air, contains 3·66 per cent. of potash, 3·87 of carbonic acid, 81·98 of uranic oxide, and 10·49 of water, and is probably only a loosely combined mixture of uranic oxide and monocarbonate of potash. (Ebelmen.) [Compare further Berzelius, p. 182.]—According to Brande, [impure] hydrated uranic oxide dissolves in aqueous carbonic acid, and on heating the liquid, is again precipitated almost entirely free from carbonic acid.

URANIUM AND BORON.

The greyish green precipitate which borax gives with protochloride of uranium, consists almost wholly of hydrated protoxide; it blackens quickly, and turns yellow after long exposure to the air. (Rammelsberg.)

BORATE OF URANIC OXIDE, OR URANIC BORATE.—Prepared by precipitating a uranic salt with borax; it is of a light yellow colour, and very sparingly soluble in water. (Richter.)

URANIUM AND PHOSPHORUS.

A. PHOSPHATE OF URANOUS OXIDE, OR URANOUS PHOSPHATE.—*Diphosphate.*—An excess of diphosphate of soda completely precipitates protochloride of uranium. The green gelatinous precipitate gives up the whole, or nearly the whole of its phosphoric acid to potash, but none to ammonia. Even when recently precipitated, it dissolves only in concentrated hydrochloric acid, and is again thrown down on the addition of water.—Pyrophosphate of soda gives the same precipitate, which, on ignition, loses 12·66 per cent. of water. (Rammelsberg.)

	Dried over oil of vitriol.		Rammelsberg.
2UO	136·0	58·02	59·62
cPO^5	71·4	30·47	
3HO	27·0	11·51	11·43
$2UO,HO,cPO^5+2Aq.$	234·4	100·00	

B. PHOSPHATE OF URANIC OXIDE, OR URANIC PHOSPHATE. ¶ *a. Triphosphate.* $3U^2O^3, PO^5$. This compound appears to exist in certain double salts. Thus, when tribasic phosphate of soda, $3NaO, PO^5$, and nitrate of uranic oxide are mixed in equal numbers of atoms, a light yellow powder is precipitated, which acquires a slight greenish tint when ignited, and retains this colour on cooling. It appears to be composed of $(U^2O^3, 2HO)\ PO^5+3U^2O^3, PO^5+xAq.$—When nitrate of uranic oxide is mixed with a moderate excess of triphosphate of soda (a very large excess would redissolve nearly the whole of the precipitate), a dark yellow precipitate is obtained, which is insoluble in water, and appears to consist of $(NaO, 2U^2O^3)\ PO^5+3U^2O^3, PO^5$. The same salt is obtained when triphosphate of soda is mixed with a quantity of uranic nitrate not sufficient to decompose the whole of it. When the triphosphate of soda is added in sufficient excess to redissolve part of the precipitate, the insoluble residue is a mixture of different salts.

b. Diphosphate.—$(2U^2O^3, HO)\ PO^5+xAq.$—1. When uranic oxide is digested in a small quantity of aqueous phosphoric acid, a yellow saline mass is produced, part of which (*c*) dissolves in boiling water, while the rest remains undissolved. The insoluble portion is an amorphous, light yellow powder, which becomes darker when ignited, but resumes its original colour on cooling. It contains 4 atoms of water, three of which are given off between 120° and 170°, and the fourth, the basic atom, at a red heat.

	Calculation.		Werther.
$2U^2O^3$	288·0	72·85	72·16
PO^5	71·4	18·05	17·96
4HO	36·0	9·10	9·66
$(2U^2O^3,HO)\ PO^5+3Aq.$	395·4	100·00	99·78

2. Phosphoric acid, added to a solution of uranic acetate, throws down a precipitate, having a distinctly crystalline character, of somewhat darker colour than the preceding, but exhibiting similar phenomena when ignited. After drying in the air at ordinary temperatures, it contains 9 atoms of water, and is composed of $(2U^2O^3, HO)\ PO^5+8Aq.$ Of these

9 atoms, two are driven off at 60°, leaving a salt composed of $(2U^2O^3, HO)PO^5+6Aq$. Of the 7 atoms of water contained in this last-mentioned compound, six are driven off at 120°, and the seventh at a red heat. The same salt with 7 atoms of water is obtained when nitrate of uranic oxide is added to a solution of ordinary diphosphate of soda $(2NaO, HO, PO^5)$ or to the mother-liquid obtained when triphosphate of soda $(3NaO, PO^5)$ is imperfectly decomposed by nitrate of uranic oxide.

	Calculation.		Werther.
$2U^2O^3$	288·0	68·19	68·10
PO^5	71·4	16·89	16·94
$7HO$	63·0	14·92	14·96
$(2U^2O^3,HO)PO^5+6Aq.$	422·4	100·00	100·00

	Calculation.		Werther.
$2U^2O^3$	288·0	65·39	65·30
PO^5	71·4	16·21	16·26
$3HO$	81·0	18·40	18·44
$(2U^2O^3,HO)PO^5+8Aq.$	440·4	100·00	100·00

(Werther, *J. pr. Chem.* 43, 321.) ¶

When phosphoric acid is added to a solution of uranic acetate, or ammonia to a solution of acid uranic phosphate, yellowish white flakes are obtained, scarcely, if at all, soluble in water, but easily soluble in carbonate of ammonia. From the latter solution they are again separated on evaporating the liquid. (Laugier, *Ann. Chim. Phys.* 24, 23.)

	Calculation.		Laugier.
$2U^2O^3$	288·0	64·09	61·0
PO^5	71·4	15·89	16·6
$10HO$	90·0	20·02	22·0
$2U^2O^3,PO^5+10Aq.$	449·4	100·00	99·6

[This result, which is not in accordance with Werther's, can scarcely be depended upon, inasmuch as the analysis differs widely from the calculation. (W.)]

c. Acid Phosphate. 1. Prepared by dissolving the diphosphate or the carbonate of uranic oxide in excess of phosphoric acid.—Not crystallizable, but forms a pasty mass, which becomes moist when exposed to the air. (Richter.)

¶ 2. The solution obtained by digesting uranic oxide in a small quantity of aqueous phosphoric acid, boiling the resulting yellow saline mass in water, and decanting from the insoluble diphosphate (*b*, 1), deposits, when sufficiently concentrated, and then left to evaporate in vacuo over oil of vitriol—a lemon-yellow salt in distinct but closely-grouped crystals, too small to be measured. These crystals, when gently heated, give off part of their water and become pale yellow. A red heat is required to expel the remainder of the water completely; but the greater part of it may be driven off by continued exposure to a temperature of 170°—200°: under these circumstances the salt swells up. It does not fuse or part with any portion of its acid even at the highest temperatures. When digested in water, it is decomposed, phosphoric acid and uranic oxide being dissolved, and a basic salt remaining behind. On dissolving it in phosphoric acid, and adding ammonia to the solution, a yellow salt containing ammonia is precipitated.

	Calculation.		Werther. (1)	(2)
U^2O^3	144·0	55·20	55·9	54·60
PO^5	71·4	27·47	26·7	27·49
$5HO$	45·0	17·33	16·8	17·20
$(U^2O^3,2HO)PO^5 + 3Aq.$	260·4	100·00	99·4	99·29

On comparing the several uranic phosphates examined by Werther, it will be seen that uranic oxide, in its relations with phosphoric acid, behaves like an oxide containing only one atom of oxygen (NaO, for example)—inasmuch as all these compounds are tribasic, the three atoms of base being made up either of $3U^2O^3$, or of $2U^2O^3$ and $1HO$, or of $1U^2O^3$ and $2HO$. So far, the composition of these salts tends to corroborate Peligot's view (p. 169) of the nature of uranic oxide. It will hereafter be seen (*chap.* 24) that the arseniates of uranic oxide exhibit the same analogy. ¶

URANIUM AND SULPHUR.

A. **PROTOSULPHIDE OF URANIUM.**—Metallic uranium combines with sulphur at the boiling-point of the latter, with evolution of light and heat. (Peligot.)—The protosulphide is prepared by passing the vapour of bisulphide of carbon over uranoso-uranic oxide heated to redness in a porcelain tube. (H. Rose, *Gilb.* 73, 139.) Hydrosulphuric acid gas, passed over ignited uranoso-uranic oxide forms nothing but uranous oxide mixed with a very small quantity of sulphide of uranium. (Arfvedson.) When uranous or uranoso-uranic oxide is heated to redness with sulphur, nearly all the sulphur escapes, according to Lecanu—and the whole of it, according to Ebelmen—while black uranoso-uranic oxide remains behind.

Protosulphide of uranium is yellowish black; when rubbed on a smooth surface, it leaves a black metallic streak. When heated in the air, it burns with a sulphurous flame, leaving uranoso-uranic oxide. (Rose.) It is but slightly acted on by hydrochloric acid; but nitric acid dissolves it even at ordinary temperatures, with separation of sulphur. (Berzelius.)

Protochloride of uranium dropped into an excess of bihydrosulphate of ammonia, disengages hydrosulphuric acid, and forms a blackish precipitate which, when washed, acquires a superficial grey tint, and behaves like a mixture of hydrated uranous oxide and sulphur. (Rammelsberg.)

The black precipitate, which alkaline hydrosulphates give with uranoso-uranic salts, is either anhydrous or hydrated $\frac{4}{3}$-*sulphide of Uranium.*—The dark-brown precipitate produced by alkaline hydrosulphates in salts of uranic oxide is either anhydrous or hydrated *Sesquisulphide of Uranium.*—According to Berzelius, the latter dissolves in an excess of the alkaline hydrosulphate, yielding a dark brown solution; it likewise dissolves sparingly in the water with which it is washed, and forms a brown solution. If exposed to the air while yet moist, it oxidizes and is soon converted into a mixture of sulphur and hydrated uranoso-uranic oxide; the oxide may be dissolved out by hydrochloric acid. If, however, during its exposure to the air, a portion of the solution containing the alkaline hydrosulphate is left in contact with it, an orange-yellow substance is produced, which Berzelius regards as a compound of sulphide of uranium and uranic oxide [or an alkaline uranate?]. The same substance is obtained when hydrosulphuric acid gas is passed through an alkaline uranate diffused in water till it acquires an orange-yellow colour (a very large excess of hydrosulphuric acid would give rise to the production of too large a quantity of brownish black sulphide of uranium). The compound dissolves in hydrochloric acid, forming a green solution, with evolution of hydrosulphuric acid gas and separation of sulphur. (Berzelius.) The sulphide of uranium, precipitated by alkaline hydrosulphates, dissolves in an aqueous solution of sulphurous acid; the yellow solution deposits the greater part of the uranium on boiling. (Berthier, *Ann. Chim. Phys.* 50, 369.)

Hydrosulphite of soda in excess gives with protochloride of uranium a greyish green precipitate, consisting of a mixture of sulphur and basic sulphite of uranous oxide, sulphurous acid being set free at the same time. (Rammelsberg.)

B. SULPHITE OF URANOUS OXIDE, OR URANOUS SULPHITE.—*Disulphite.*—Monosulphite of soda gives with protochloride of uranium, a greyish green precipitate, the formation of which is attended with disengagement of sulphurous acid. When the sulphite of soda is in excess, the filtrate still retains a portion of the salt in solution, the liquid having a green colour; after long standing, however, sulphurous acid is evolved, and the salt again deposited. When heated, the salt loses water and sulphurous acid, and leaves uranous oxide, or, if air is present, uranoso-uranic oxide. It dissolves readily in acids. (Rammelsberg.)

	Dried over oil of vitriol.		Rammelsberg.
$2UO$	136	73·12	72·03
SO^2	32	17·20	16·60
$2HO$	18	9·68	
$2UO,SO^2+2Aq.$	186	100·00	

C. SULPHITE OF URANIC OXIDE, OR URANIC SULPHITE.—$U^2O^3,SO^2+3Aq.$—Precipitated as a yellow granular powder, on boiling a solution of carbonate of uranic oxide and ammonia in a solution of sulphurous acid or a uranic salt with sulphite of ammonia. (Berthier.) ¶ Flocculent precipitate, permanent in the air, but resolved by heat into sulphurous acid and a brown residue, probably consisting of a mixture of uranous and uranic oxides. It may also be prepared by passing a current of sulphurous acid through hydrated uranic oxide diffused in water.

	Calculation.		Muspratt.
U^2O^3	144	70·89	71·72
SO^2	32	15·82	14·70
$3HO$	27	13·28	13·58
$U^2O^3,SO^2+3Aq.$	203	100·00	100·00

(Muspratt, *Ann. Pharm.* 50, 259.) ¶

D. SULPHATE OF URANOUS OXIDE, OR URANOUS SULPHATE.—*a. Disulphate.*—1. Remains as an insoluble residue on treating the normal salt with a large quantity of water. (Peligot.)—2. A solution of monosulphate of uranic oxide in dilute alcohol, exposed to the sun's rays, becomes colourless, and deposits the basic salt, at the same time emitting an odour of aldehyde. (Ebelmen.)—3. An aqueous solution of the normal salt is boiled with green uranoso-uranic oxide, and the liquid decanted while still hot from the salt *a* thereby produced, because it redissolves on cooling. (Ebelmen.)—4. By careful addition of ammonia to a solution of the normal salt, the salt *a* is precipitated. (Rammelsberg.)—The salt is collected on a filter, washed with a small quantity of cold water, and dried. —It forms a light green powder, sometimes having a silky lustre. (Peligot, Ebelmen.) Large quantities of water (especially if boiling) successively added to the salt, continually abstract sulphuric acid, free from uranium, and turn the salt black. (Ebelmen.)

	Dried in vacuo over oil of vitriol.		Ebelmen.	Rammelsberg.
$2UO$	136	70·10	71·53	68·31
SO^3	40	20·62	19·17	19·99
$2HO$	18	9·28	9·30	
$2UO,SO^3+2Aq.$	194	100·00	100·00	

Ebelmen found too large a proportion of base and too little acid, because, according to his own statement, the salt was partially decomposed, even during washing. The salt examined by Rammelsberg lost 9·77 per cent. of water at 220°. Rammelsberg supposes it to contain 3 atoms of water.

b. Monosulphate.—Found native as *Uranium-vitriol.*—1. Formed by dissolving uranous oxide in boiling oil of vitriol. (Rammelsberg). Or by dissolving green uranoso-uranic oxide in excess of hot oil of vitriol, diluting the solution with water, and evaporating in vacuo. The uranous sulphate then crystallizes out, provided the acid is in considerable excess, leaving the uranic sulphate in solution. Crystals are still more readily obtained by mixing the solution of uranoso-uranic oxide in an excess of sulphuric acid,, with water and a small quantity of alcohol, and exposing the whole in a stoppered bottle to the sun's rays. The alcohol, which is itself converted into aldehyde, converts the uranic salt present into a uranous salt, which then crystallizes on the sides of the vessel. The clear liquid (which by evaporation and cooling may be made to yield more crystals) is poured off, and the crystals are dried in the air on bibulous paper. (Ebelmen.)—2. A concentrated aqueous solution of protochloride of uranium, treated with sulphuric acid, solidifies in consequence of the separation of crystallized uranous sulphate; on the application of heat, the hydrochloric acid is evolved, and a greenish jelly left, which is then to be nearly evaporated to dryness, redissolved in water, and the solution set aside to crystallize. (Peligot.)

α. Bi-hydrated.—This salt forms green crystals permanent in the air. (Ebelmen.)

β. Tetra-hydrated.—Crystallizes in green prisms, which are permanent in the air, and belong to the right prismatic system of crystallization. —Faces *u*, *m*, *t*, and *a*; the form is therefore a right rhombic prism, converted by the truncation of the lateral edges into an octagonal prism, in which the truncation-face *m*, which replaces the obtuse lateral edge, is the largest; acuminated with the four *a*-faces, of an obtuse rhombic octohedron, resting upon *u*; the obtuse edges of the latter are truncated by two faces resting upon *m*; the more obtuse = 167° 14′ (166° 30′ Prevostaye); $u' : u = 118° 38'$. (Rammelsberg.)—(*Vide* Prevostaye's more elaborate description, *N. Ann. Chim Phys.* 5, 48.)

The salt when ignited leaves black uranoso-uranic oxide. It is converted, [by more gentle ignition?] in the air, into sulphate of uranic oxide, with evolution of sulphuric acid vapours. Ignited in a current of hydrogen gas, it leaves uranous oxide free from sulphuric acid. (Ebelmen.) The crystals, when heated slowly, part with their water. At 200°, they still retain a sixth part; at 230° they lose 21·34 per cent.; and, at a temperature approaching to redness, the residual portion is evolved, together with a small portion of sulphuric acid, so that the loss amounts to 26·35 per cent.; the yellow residue, after prolonged ignition, leaves blackish green uranoso-uranic oxide. (Rammelsberg.)—Water decomposes the crystals into the insoluble basic salt and a green acid solution. (Peligot.) The solution absorbs oxygen in the air, and rapidly turns yellow from formation of uranic sulphate, the precipitated disulphate of uranous oxide being redissolved at the same time. (Ebelmen.) The crystals dissolve readily and completely in dilute sulphuric or hydrochloric acid. (Ebelmen.) If, however, the excess of acid is but small, the solution becomes turbid by heat. (Rammelsberg.) A small quantity of ammonia precipitates the disulphate from an aqueous solution; a larger addition of ammonia throws down hydrated uranous oxide. (Rammelsberg.)—Concentrated sulphuric or hydrochloric acid dissolves the salt but very sparingly, and consequently precipitates it from an aqueous solution in the crystalline form. (Ebelmen, Rammelsberg.)

	a		Ebelmen.
UO	68	53·97	53·02
SO^3	40	31·74	31·85
2HO	18	14·29	15·13
$UO,SO^3+2Aq.$	126	100·00	100·00

	β		Peligot.	Rammelsberg.
UO	68	47·22	46·3	46·19
SO^3	40	27·78	29·7	27·91
4HO	36	25·00	24·0	
+4Aq.	144	100·00	100·0	

Peligot probably allowed his crystals to separate from a solution containing a larger quantity of acid, so that they combined with less water. In more recent analyses, Rammelsberg found only between 44·98 and 45·81 per cent. of uranous oxide. Every analysis gives a small deficiency of uranous oxide and an excess of acid, in consequence of the salt being crystallized from an acid solution.

E. SULPHATE OF URANOSO-URANIC OXIDE, or URANOSO-URANIC SULPHATE.—On dissolving green uranoso-uranic oxide in warm oil of vitriol, and expelling the excess of acid in a platinum crucible, a pale green mass is obtained, which may be regarded as $U^3O^4, 2SO^3$ or as $UO, SO^3+U^2O^3,SO^3$.—This salt, when ignited, evolves sulphurous acid, and leaves pale yellow sulphate of uranic oxide. $2(U^3O^4, 2SO^3)=3(U^2O^3, SO^3)+SO^2$.—It is soluble in water, and forms a green solution; this liquid when boiled, deposits uranous sulphate, which redissolves as the liquid cools. (Ebelmen.) Alcohol likewise precipitates uranous sulphate from the liquid, leaving uranic sulphate in solution. (Berzelius.)

	Pale green mass.		Ebelmen.	Or:		
U^3O^4	212	*72·6*	72	UO,SO^3	108	36·98
$2SO^3$	80	*27·4*	28	U^2O^3,SO^3	184	63·02
$UO,SO^3+U^2O^3,SO^3$	292	100·0	100		292	100·00

F. Sulphate of Uranic Oxide, or Uranic Sulphate.—*a. Basic sulphate.*—Found native, according to Berzelius, in the form of a yellow powder.

b. Monosulphate.—1. A solution of uranoso-uranic oxide in oil of vitriol is diluted with a moderate quantity of water and oxidized by nitric acid. (Arfvedson.)—2. An aqueous solution of uranic nitrate is evaporated to dryness with sulphuric acid; the excess of acid expelled by heat; the residue dissolved in water; and the solution evaporated to a syrupy consistence, and left to itself for some time, in order that it may deposit crystals. (Ebelmen.) The crystallization is attended with difficulty. Small lemon-yellow prisms (Bucholz); sometimes yellow, sometimes green crystals, which redden litmus, even when fully saturated with uranic oxide. (Lecanu.)

	Calculation.		Bucholz.	Ebelmen.
U^2O^3	144	68·25	70	66·74
SO^3	40	18·96	18	18·60
3HO	27	12·79	12	14·66
$U^2O^3,SO^3 + 3Aq$	211	100·00	100	100·00

Ebelmen estimates the quantity of water in the crystals not at 3, but at 3½ atoms. According to his statement, they part with ½ at. water when exposed to the air for a long time. Possibly, however, a portion of the syrupy mother-liquid adhered to the salt which Ebelmen examined, and this liquid afterwards dried up to a crystalline salt.

The crystals when heated to 100°, retain only one atom of water, which begins to escape at 150°, and is wholly driven off at 300°; the residue afterwards absorbs 3 atoms of water from the air. (Ebelmen.) When ignited, the crystals leave 64 per cent. of uranoso-uranic oxide, containing a small quantity of sulphuric acid. (Bucholz.) When heated to redness in a current of hydrogen gas, the salt yields water and sulphurous acid, and afterwards hydrosulphuric acid and sulphur, leaving uranous oxide free from sulphur. (Ebelmen.) An alcoholic solution of the salt, exposed to the sun's rays, deposits the whole of the uranium in the form of uranous sulphate. (Bucholz, Ebelmen.)—One part of the salt dissolves in 0·6 parts of cold water, forming a thin syrup, and in 0·45 parts of boiling water; in 25 parts of cold, and in 20 parts of boiling absolute alcohol (Bucholz); it dissolves in 0·47 parts of water at 21°, and in 0·28 parts of boiling water. (Ebelmen.)

c. Bisulphate.—$U^2O^3,2SO^3$.—Separates from a solution of the mono-acid salt in dilute sulphuric acid, in crystals resembling those of Wavellite. (Berzelius.)

d. Tersulphate.—$U^2O^3,3SO^3$.—Crystallizes from a solution of the salt *b* or *c*, in oil of vitriol. (Berzelius.)—¶ Peligot (*N. Ann. Chim. Phys.* 12, 558,) denies the existence of the two latter salts, inasmuch as by following the methods of Berzelius, he succeeded only in obtaining, in the first instance, a variable compound, which he regarded as a mixture of the monosulphate and acid sulphate; and in the second, a deliquescent salt, containing 58·0 per cent. of uranic oxide, 36·9 of sulphuric acid and 5·1 of water, which nearly corresponds to the formula $U^2O^3,2SO^3,HO$ (a salt similar in composition to the bisulphate of potash). The excess of sulphuric acid arises from the impossibility of removing the whole of the mother-liquid. ¶

G. Hydrosulphocarbonate of lime forms with uranic salts, a dark-brown liquid, which gradually becomes turbid, and deposits a pale greyish brown precipitate. The latter appears to be a compound of *Bisulphide of Carbon* with *Sesquisulphide of Uranium;* the solution, however, continues yellow. (Berzelius.)

Uranium and Selenium.

Selenite of Uranic Oxide, or Uranic Selenite.—*a. Monoselenite?*—Lemon-coloured powder, which is converted by heat into green uranoso-uranic oxide, with loss of selenious acid and oxygen gas.

b. Acid selenite?—Prepared by dissolving *a* in an aqueous solution of selenious acid. When imperfectly dried, it is transparent and of the consistence of varnish; in the anhydrous state it is white, opaque, and crystalline. Soluble in water. (Berzelius.) Its formula, according to Muspratt, is $U^2O^3, 3SeO^2$.

Uranium and Iodine.

A. Proto-iodide of Uranium and Hydriodate of Uranous Oxide.—Hydrated protoxide of uranium yields with aqueous hydriodic acid, a dark green solution containing free hydriodic acid. When spontaneously evaporated, the solution turns brown and evolves free iodine, leaving a black crystalline mass, which contains a small quantity of sesqui-iodide of uranium, and dissolves in water, forming a brownish-red solution. (Rammelsberg.)

B. Iodate of Uranous Oxide, or Uranous Iodate.—Iodate of soda gives with protochloride of uranium, a pale green precipitate which is soluble in an excess of the latter salt. The precipitate, if allowed to remain immersed in the liquid, is converted, after some time, into white iodate of uranic oxide, of which a portion dissolves, together with free iodine in the solution, and colours it yellow. (Rammelsberg.)

C. Iodate of Uranic Oxide, or Uranic Iodate.—Iodic acid and iodate of potash produce in a solution of uranic nitrate, a white precipitate, soluble in a large quantity of water. (Pleischl.) The salt, which is yellowish white when dried, gives off part of its water of crystallization at the temperature at which decomposition commences; it then evolves iodine and oxygen gas, and leaves uranoso-uranic oxide. It gives up its acid to potash, and dissolves with some difficulty in nitric acid. (Rammelsberg.)

	Calculation.		Rammelsberg.
U^2O^3	144	40·56	40·13
IO^5	166	46·76	
5HO	45	12·68	
$U^2O^3,IO^5 + 5Aq.$	355	100·00	

Periodate of potash gives with protochloride of uranium, a greyish green precipitate of *Periodate of Uranous oxide,* which, after some time, is converted into yellowish white periodate of uranic oxide; the latter dissolves in the liquid on the application of heat. (Rammelsberg.)

URANIUM AND BROMINE.

A. PPOTOBROMIDE OF URANIUM.—*Hydrated*, or *Hydro-bromate of Uranous oxide.*—The dark green solution of hydrated uranous oxide in aqueous hydrobromic acid, evaporated over oil of vitriol, yields ill-defined dark green crystals, and dries up to a highly deliquescent saline mass. The aqueous solution gives off hydrobromic acid when heated, and deposits a fine black powder, probably consisting of uranous oxide. (Rammelsberg.)

	Calculation.		Rammelsberg.
U	60·0	34·40	34·43
Br	78·4	44·96	
4HO	36·0	20·64	
UBr,4Aq.	174·4	100·00	

B. BROMIDE OF URANOUS OXIDE and MONOHYDROBROMATE OF URANIC OXIDE.—2UO,Br and U^2O^3,HBr.—By boiling uranous oxide with bromine and water, or by dissolving uranic oxide in aqueous hydrobromic acid, a colourless solution is obtained, which turns yellow when evaporated, and yields flat yellow needles having a strong styptic taste. When dried at a high temperature, these crystals assume an orange colour and evolve hydrobromic acid; at a red heat, they evolve bromine and leave uranic oxide (uranoso-uranic oxide). They deliquesce in the air; ammonia precipitates uranic oxide from their solution. (Berthemot, *Ann. Chim. Phys.* 44, 387.)

The green mixture of protochloride of uranium and bromate of potash immediately turns yellow, from formation of sesquibromide of uranous oxide and separation of free bromine. (Rammelsberg.)

C. BROMATE OF URANIC OXIDE OR URANIC BROMATE.—When monosulphate of uranic oxide is precipitated by bromate of baryta in equivalent proportions, and the yellow filtrate allowed to evaporate under a bell-jar over oil of vitriol, a clear uncrystallizable syrup remains, which, on exposure to the heat of a water-bath, evolves a considerable quantity of bromine, and then solidifies. The mass dissolves in water, with the exception of a small quantity of a brown powder; the solution again evaporated and digested in water till the residue dissolves completely, yields, on evaporating the solution and drying the residue under a receiver over oil of vitriol, a yellow pulverulent salt. The latter when heated out of contact of air yields water, oxygen gas, vapour of bromine, and a yellow residue containing bromide of uranium [dibromide of uranous oxide?] and when ignited in the air, leaves uranoso-uranic oxide. (Rammelsberg, *Pogg.* 55, 77.)

The yellow salt.	Approximate calculation.		Rammelsberg.
$4U^2O^3$	576·0	53·57	53·77
$3BrO^5$	355·2	33·03	32·23
16HO	144·0	13·40	14·00
$4U^2O^3,3BrO^5 + 16Aq$	1075·2	100·00	100·00

URANIUM AND CHLORINE.

A. THREE-FOURTHS CHLORIDE OF URANIUM.—Formed by passing dry hydrogen gas over protochloride of uranium heated in a tube till it nearly volatilizes, as long as hydrochloric acid continues to be formed.

$$4UCl + H = U^4Cl^3 + HCl.$$

Dark brown mass, of coarse fibrous texture, and but slightly volatile.—Dissolves very readily in water. The purple solution is converted in a few moments—with evolution of hydrogen gas and separation of a red powder, which is probably an oxide of uranium—into a green solution of protochloride of uranium. (Peligot.) [The behaviour of the aqueous solution, prepared as above with ammonia is described with the suboxides of uranium. (p. 159).] According to Rammelsberg, the same chloride of uranium is obtained by igniting the protochloride in ammoniacal gas.

	Calculation.		Peligot.
4U	240·0	69·33	69·1
3Cl	106·2	30·67	30·6
U^4Cl^3	346·2	100·00	99·7

B. PROTOCHLORIDE OF URANIUM.—Dry hydrochloric acid gas has no action on uranous oxide at a red heat.—Uranium burns in chlorine gas with vivid incandescence, yielding protochloride of uranium.—*Preparation.*—Dry chlorine gas is passed over an intimate mixture of charcoal and either of the oxides of uranium heated in a very refractory glass tube. The heat is applied gently at first, in order to expel the moisture, and the chlorine is made to pass slowly through the tube; but afterwards the heat is greatly inreased, and the chlorine made to pass over in larger quantities. The chloride of uranium which volatilizes in red vapours, in company with carbonic acid and chlorine gas, condenses in the tube not far from the heated portion. The tube is then fused between the chloride of uranium and the charcoal, and likewise at the other extremity. (Peligot.) The quantity of charcoal should not exceed one-fourth the weight of the uranoso-uranic oxide; the chloride of uranium, which for the most part condenses close to the mixture, is then contaminated with but a small quantity of charcoal. Where the chlorine first comes in contact with the mixture, large acicular crystals of chloride of uranous oxide are formed. (Rammelsberg.)

Chloride of uranium crystallizes in dark green regular octohedrons, which have the metallic lustre; and, when heated to redness, volatilize in red vapours and sublime. (Peligot.)

	Calculation.		Peligot (*mean*).	Rammelsberg.
U	60·0	62·89	61·14	
Cl	35·4	37·11	37·86	35·983
UCl	95·4	100·00	99·00	

Peligot obtained, as the average of six analyses, 71·333 per cent. of uranoso-uranic oxide; if this be estimated as U^4O^5, it gives 280 : 240 = 71·333 : 61·14; consequently 61·14 of uranium, and not 62·9, as in Peligot's calculation.

Hydrated Chloride of Uranium or *Mono-hydrochlorate of Uranous Oxide.*—1. Protochloride of uranium when exposed to the air emits a cloud of hydrochloric acid, and still more powerfully on the addition of water, because a rise of temperature is thereby produced: it is very easily soluble in water. (Peligot.)

Dissolves in water with a hissing noise. (Rammelsberg.) The dark emerald-green solution loses a considerable quantity of hydrochloric acid when evaporated, and leaves an amorphous residue, which is perfectly soluble in water, and, when strongly ignited in an open vessel, is converted into uranoso-uranic oxide. When evaporated in vacuo, the solution also leaves a green, uncrystallizable, resinous, deliquescent mass, different from protochloride of uranium. (Peligot.)

The green solution of protochloride of uranium turns brown when boiled and evaporated, giving off hydrochloric acid and depositing a very fine black powder, which passes through the filter, and appears to consist of uranous oxide: the brown colour is retained for twenty-four hours; ammonia precipitates hydrated uranous oxide from the brown as well as from the green solution. (Berzelius.) The hydrate, on being washed in the air, is converted into hydrated uranoso-uranic oxide. (Rammelsberg.) —2. An ethereal solution of hydrochlorate of uranic oxide exposed to the direct rays of the sun, becomes colourless and deposits hydrochlorate of uranous oxide in green flakes, which unite into a blackish green unctuous mass, and dissolve with the same colour in water. (Gehlen, *A. Gehl.*, 3, 569.)

C. Hydrochlorate of Uranoso-uranic Oxide.—Concentrated hydrochloric acid forms with green uranoso-uranic oxide a bottle-green solution, which becomes paler in the air, in consequence of the formation of a uranic salt, and dries up to an uncrystallizable mass. (Arfvedson.)

D. Chloride of Uranous Oxide.—*Peligot's Chloride of Uranyl.*—When dry chlorine gas is passed over uranous oxide at a red heat, the tube becomes filled with an orange-yellow vapour of chloride of uranous oxide. (Peligot.)

$$2UO + Cl = 2(UO),Cl.$$

If the protoxide contains any uranoso-uranic oxide, sesquioxide of uranium remains behind on dissolving the compound. (Peligot.)—Chloride of uranous oxide is yellow, crystalline, readily fusible, and apparently not very volatile.—When heated with potassium, it is resolved into chloride of potassium and uranous oxide:

$$2UO,Cl + K = 2UO + KCl.$$

It is highly deliquescent. (Peligot.)

	Calculation.		Peligot (*mean*).
2UO	136·0	79·34	79·6
Cl	35·4	20·66	20·4
2UO,Cl	171·4	100·00	100·0

This compound may be regarded: (1) with Peligot, as $U^2O^2 + Cl$, that is to say as chloride of uranyl; (2) with Berzelius, as $2U^2O^3,U^2Cl^3$, or as a compound of 2 atoms of uranic oxide with one atom of sesquichloride of uranium; (3) as U^2O^2Cl, or as uranic oxide in which the third atom of oxygen is replaced by chlorine. At all events, this compound is analogous to COCl, SO^2Cl, and CrO^2Cl.

E. MONO-HYDROCHLORATE OF URANIC OXIDE.—1. Prepared by dissolving chloride of uranous oxide in water:

$$U^2O^2Cl + HO = U^2O^3,HCl.$$

—2. Hydrochlorate of uranous or uranoso-uranic oxide is oxidized by exposure to the air, or by nitric acid.—According to Klaproth, the yellow solution yields, on evaporation, yellowish green crystals, which effloresce in the air, and are readily soluble in water, alcohol, and ether, and appear to be oblique four-sided tables. According to Lecanu, the solution yields a few very deliquescent needles, which scarcely redden litmus. According to Arfvedson, the solution dries up to an uncrystallizable, highly deliquescent syrup.

F. CHLORATE OF URANOUS OXIDE OR URANOUS CHLORATE.—The green solution of hydrated uranous oxide in aqueous chloric acid decomposes spontaneously (very quickly when heated), chlorine being evolved, and the liquid assuming a yellow colour, from formation of hydrochlorate of uranic oxide. (Rammelsberg.)

G. PERCHLORATE OF URANOUS OXIDE.—The dark green solution of the hydrate in aqueous perchloric acid cannot be evaporated to dryness either over oil of vitriol or over a water-bath, because it is thereby partially converted into hydrochlorate of uranic oxide. (Rammelsberg.)

URANIUM AND FLUORINE.

FLUORIDE OF URANIUM and HYDROFLUATE OF URANIC OXIDE.—The yellow solution of uranic oxide in aqueous hydrofluoric acid yields on evaporation a white, amorphous, pulverulent crust, which creeps up the sides of the containing vessel: after being completely dried, it redissolves in water without change. With alkaline fluorides, fluoride of uranium forms yellow crystallizable compounds soluble in water. (Berzelius, *Pogg.* 1. 34.)

URANIUM AND NITROGEN.

A. NITRATE OF URANIC OXIDE OR URANIC NITRATE.—*a. Basic nitrate.* —Formed by gently heating the normal salt till it assumes an orange-yellow colour, after which the still undecomposed mononitrate (together with a small quantity of basic salt) is removed by washing with water. —Yellow powder insoluble in water containing 0·92 of oxide. (Bucholz.) Orange-yellow; leaves when ignited first U^3O^4, and then U^4O^5. (Peligot.)

b. Mononitrate.—Uranous, uranoso-uranic, or uranic oxide is dissolved in dilute nitric acid, and the solution evaporated to the crystallizing point. [For Peligot's and Ebelmen's mode of preparation, vid. p. 163.] —The salt crystallizes in lemon-yellow prisms (Bucholz) with a tinge of green; the crystals redden litmus. (Lecanu.) Crystalline system, the right prismatic.—Form: rectangular prism (*m*- and *t*-faces) acuminated with the *a*-faces of a rhombic octohedron, the apex replaced by the *p*-face.

$a : m = 125°$; $a : t = 116° 30'$. (Haberle, *A. Gehl.* 4, 146.) Also with the i-faces. $a : t = 116° 30'$; $i : t = 121° 20'$; $i : m = 120° 45'$; $i : i = 117° 20'$; $a : u = 127$. (Prevostaye, *N. Ann. Chim. Phys.* 5, 48.)

	Calculation.		Peligot.	Kühn.
U^2O^3	144·0	57·14	57·05	58·57
NO^5	54·0	21·43	21·46	21·38
6HO	54·0	21·43	22·50	
$U^2O^3,NO^5 + 6Aq.$	252·0	100·00	101·01	

The crystallized salt remains unaltered in the air at temperatures between 15° and 20°. (Lecanu.) In a warm dry atmosphere it effloresces to a yellow powder (Bucholz); also in vacuo, with loss of 3 atoms of water. (Peligot.) When heated, it melts in its own water of crystallization, gives off water and acid, and acquires a reddish yellow colour, and when heated to redness, is converted into uranoso-uranic oxide. (Bucholz.) If the salt be fused at a gentle heat, till the greater part of the water is expelled, a yellow liquid remains, which, on cooling, solidifies in transparent prisms; and these, when exposed to the air, rapidly absorb water and lose their transparency. (Peligot.) According to Arfvedson, the salt evolves oxygen when moderately heated and is converted into nitrite of uranic oxide, which, at incipient redness, is decomposed into nitrous acid gas and uranoso-uranic oxide, without the intermediate production of pure uranic oxide. The salt fuses on ignited charcoal and then detonates like nitre. (Lecanu.) An alcoholic solution, heated to a temperature of 38°, evolves heat spontaneously, boils with the greatest violence, gives off nitrous ether, and deposits a very large quantity of a lemon-yellow powder, which appears to be nearly pure uranic oxide. (Bucholz; see also Malaguti, p. 168.) When a solution of uranic nitrate in sulphuric ether is exposed to sun-light, nitrous ether is produced, a large quantity of uranic oxide deposited, and there remains an aqueous solution coloured green by a salt of uranous oxide. (Bucholz.) The salt dissolves in half its weight of cold water, forming a greenish yellow solution; it deliquesces in a moist atmosphere. It is also soluble in 0·3 parts of absolute alcohol, and dissolves readily in sulphuric ether. (Bucholz.)

c. Ternitrate.—$U^2O^3, 3NO^5$.—This salt crystallizes with greater facility, and is less soluble in water than *b*; it likewise effloresces in the air. (Berzelius.) According to Lecanu, a solution of uranic oxide in excess of nitric acid, yields on evaporation a beautiful green, amorphous mass, which deliquesces in the air. According to Ebelmen, there is no salt containing more than one atom of NO^5 to one atom of U^2O^3. ¶ This statement is also confirmed by Peligot, (*N. Ann. Chim. Phys.* 12, 557,) who succeeded only in obtaining the ordinary nitrate with 6 atoms of water. ¶

B. Uranate of Ammonia.—Precipitated in the hydrated state as a yellow powder, on mixing hydrochlorate or nitrate of uranic oxide with excess of ammonia. The salt remains unchanged even at temperatures above 100°, but when exposed to a stronger heat, it gives off nitrogen gas, ammonia, and water, and is converted into uranous oxide. Does not dissolve in excess of ammonia. (Arfvedson.) Sparingly soluble in pure water, but insoluble in water containing sal-ammoniac. (Berzelius.)

—Contains 90 per cent. of uranic oxide.—Cannot be freed from ammonia by boiling with water.—Dissolves in sesquicarbonate of ammonia, forming a solution of the following salt D. (Peligot.)

C. CARBONATE OF URANOUS OXIDE AND AMMONIA.—*Uranoso-ammonic Carbonate.*—Carbonate of ammonia gives with uranous salts a dark green precipitate, which dissolves in an excess of the precipitant, forming a dark green solution. The solution, evaporated at a gentle heat, evolves carbonic acid, and deposits first hydrated uranous oxide, and then uranate of ammonia. (Rammelsberg.) The pale green precipitate which ammonia produces in a solution of uranoso-uranic sulphate likewise dissolves in excess of the former, producing a pale green solution. This liquid, when heated, deposits the uranoso-uranic oxide free from carbonic acid. (Arfvedson.)

D. CARBONATE OF URANIC OXIDE AND AMMONIA.—*Urano-ammonic Carbonate.*—*a. Neutral Salt.*—Carbonate of uranic oxide, or uranate of ammonia, is dissolved in a warm aqueous solution of sesquicarbonate of ammonia and the lemon-yellow filtrate left to cool till it crystallizes (Berzelius); or the solution is spontaneously evaporated. (Lecanu, Peligot.)—Ebelmen digests an excess of uranate of ammonia with carbonate of ammonia at temperatures between 60° and 70°, filters warm, and sets the solution aside to crystallize. The uranate of ammonia which remains undissolved, may again be treated with the mother-liquid. Delffs (*Pogg. 55, 229,*) agitates the uranate of ammonia for some minutes in a stoppered bottle, at a temperature of 35°, with a concentrated solution of carbonate of ammonia; filters, without diluting the filtrate with the wash-water, and sets aside to cool.

Crystallizes in lemon-yellow transparent prisms, which are permanent in the air. (Berzelius, Lecanu, Peligot.)—Sulphur-yellow and opaque. (Delffs.) Crystalline system, the oblique prismatic. *Fig.* 85, with the *m*-face; the *f*-face larger; $\alpha : t = 138^\circ\ 45'$; $\alpha : u = 150^\circ$; $i : t = 90^\circ$; $i : f$ backwards $= 96^\circ$; $t : u^1 = 132^\circ\ 30'$; $u^1 : m = 137^\circ\ 30'$; $u^1 : u = 95^\circ$; $m : t = 90^\circ$. (Prevostaye, *N. Ann. Chim. Phys.* 5, 49.)

	Crystallized.		Ebelmen.	Delffs.	
				a.	*b.*
$2NH^3$	34	12·98	12·63	11·33	11·80
U^2O^3	144	54·96	54·89	55·47	57·19
$3CO^2$	66	25·19	25·43	23·98	24·72
$2HO$	18	6·87	7·76	9·22	6·29
$2(NH^4O,CO^2) + U^2O^3,CO^2$	262	100·00	100·71	100·00	100·00

Column *a* is the analysis by Ebelmen and Delffs of the salt dried in the air at ordinary temperatures; but as Delffs found that the latter lost 3 per cent. at 100°, and regarded the loss only as water, he calculated the analysis *b* accordingly.

The salt may be preserved in stoppered bottles, which, however, when opened, emit a smell of carbonate of ammonia; also in atmospheric air containing a small quantity of carbonate of ammonia vapour. In the open air it is very slowly decomposed, acquiring at the same time a slight orange colour. At 100°, it suffers a considerable loss of weight in a few hours; between 200°, and 250° it rapidly evolves water and carbonate of ammonia, and acquires an orange colour. The last portions of carbonate of ammonia are expelled with difficulty; but by prolonged heating, at a temperature of 300°, a residue of pure, brick-red uranic oxide is obtained. When rapidly heated in close vessels, the salt leaves protoxide of uranium, which, if exposed to the air immediately after cooling, takes fire and burns to green uranoso-uranic oxide. (Ebelmen.) When heated it gives off carbonate of ammonia, and leaves, first, carbonate uranic oxide, and then green uranoso-uranic oxide. (Peligot.)—The salt dissolves in 20 parts of water at 15°, and more abundantly in water containing carbonate of ammonia (Ebelmen); it is insoluble in pure water, but dissolves in water containing carbonate of ammonia. (Berzelius.) The solution, on being boiled, evolves carbonate of ammonia and becomes turbid, gradually depositing the compound *b*; nevertheless, a portion of uranium remains undissolved. (Arfvedson.) The aqueous solution is turned brown by hydrosulphate of ammonia, but not till after a considerable lapse of time. (Wittstein.)

b. With a very large excess of Uranic oxide?—1. The pale yellow precipitate, which appears on boiling an aqueous solution of the preceding salt *a*. On washing the precipitate, the water takes up a portion of the uranic oxide, which is again precipitated as it mixes with the saline liquid previously passed through the filter. (Arfvedson.)—According to Arfvedson, the compound contains uranic oxide with a small quantity of ammonia and carbonic acid; according to Peligot, it is uranate of ammonia; according to Ebelmen, it is hydrated uranic oxide, still containing 2 per cent. of ammonia, but no carbonic acid.—2. On precipitating nitrate of uranic oxide with carbonate of ammonia, not in excess, a yellow precipitate is obtained, which becomes lighter when washed, and at last dissolves sparingly, forming a yellow solution: this solution, when boiled, becomes yellow and milky, from separation of uranic oxide.—The above precipitate dissolves in acids with effervescence; but when heated alone, evolves water, carbonic acid, and nitrogen gas, the latter arising from decomposition of ammonia. (Berzelius, *Pogg.* 1, 361.)

E. SULPHATE OF URANOUS OXIDE AND AMMONIA.—*Uranoso-ammonic sulphate.*—Crystallizes in small dark green needles, united together in rounded masses and easily soluble in water. The solution when heated becomes turbid, from separation of basic salt; when boiled with potash, it gives off ammonia and deposits uranous oxide. (Rammelsberg.)

	Crystallized.		Rammelsberg.
NH^3	17	9·77	9·09
UO	68	39·08	41·73
$2SO^3$	80	45·98	43·15
HO	9	5·17	
NH^4O,SO^3+UO,SO^3	174	100·00	

As the salt analyzed was mixed with portions of the following compound, the analysis does not quite accord with the calculation. (Rammelsberg.)

F. SULPHATE OF URANIC OXIDE AND AMMONIA.—*Urano-ammonic Sulphate.*—Formed by mixing sulphate of uranic oxide with sulphate of ammonia, and evaporating the solution to the crystallizing point. (Arfvedson.) The salt belongs to the oblique prismatic system. (*Fig.* 102, without the faces *a* and *b*, and without the two faces between *i* and *t*); $i : t = 137°$

to 138°; $i : u = 103^\circ\ 30'$; $u : t = 109^\circ\ 40'$, &c. (Prevostaye, *N. Ann. Chim. Phys.* 5, 51.) When heated to redness, it leaves uranoso-uranic oxide; it is readily soluble in water. (Arfvedson.) Sparingly soluble. (Peligot.)

	Crystallized.			Peligot.
NH^3	17	....	6·34	
U^2O^3	144	....	53·73	53·7
$2SO^3$	80	....	29·85	29·8
$3HO$	27	....	10·08	
$NH^4O,SO^3 + U^2O^3,SO^3 + 2Aq.$	268	....	100·00	

G. Ammonio-chloride of Uranium.—100 parts of protochloride of uranium at ordinary temperatures, absorb 5·44 parts of ammoniacal gas, the action being attended with evolution of heat. (Rammelsberg.)

	Calculation.		
NH^3	17·0	....	5·61
$3UCl$	286·2	....	94·39
$3UCl,NH^3$	303·2	....	100·00

H. Chloride of Uranous Oxide and Ammonium, or Hydrochlorate of Uranic Oxide and Ammonia.—Peligot's *Ammonio-chloride of Uranyl.*—An aqueous mixture of sesqui-chloride of uranium and salammoniac evaporated to a syrupy consistence, yields, after long standing, highly deliquescent rhombohedral crystals. (Peligot.)

Calculation, according to Peligot.

	a.			Or:	*b.*		
NH^4	18·0	....	7·41	NH^3	17·0	....	7·00
U^2O^2	136·0	....	56·02	U^2O^3	144·0	....	59·31
$2Cl$	70·8	....	29·16	$2HCl$	72·8	....	29·98
$2HO$	18·0	....	7·41	HO	9·0	....	3·71
	242·8	....	100·00		242·8	....	100·00

According to *a*, $NH^4Cl + U^2O^2,Cl, + 2Aq$; according to *b*, $NH^3,HCl + U^2O^3,HCl + Aq.$

URANIUM AND POTASSIUM.

Uranoso-uranic oxide heated with potassium forms a mass which inflames spontaneously in the air. (Berzelius.)

A. Uranate of Potash.—1. Precipitated on mixing a salt of uranic oxide with excess of potash, in the form of a light orange-yellow powder, which, when ignited, loses water and becomes yellowish red. (Arfvedson.)—2. Likewise formed by fusing uranic oxide with excess of carbonate of potash, and removing the latter by water. (Berzelius.)—3. Remains in the form of a brick-red powder after igniting the double carbonate of uranic oxide and potash and exhausting with water. (Berzelius.)—4. By igniting the double acetate of uranic oxide and potash. (Wertheim.)

	Calculation.			Berzelius.	Wertheim.
KO	47·2	....	14·08	12·8	13·99
$2U^2O^3$	288·0	....	85·92	86·8	85·73
$KO,2U^2O^3$	335·2	....	100·00	99·6	99·72

When this salt is heated to redness in an atmosphere of hydrogen gas, it is partially reduced, and a mixture is formed consisting of uranoso-uranic oxide, and uranate of potash containing a larger proportion of base. The latter compound is insoluble in water, but dissolves in hydrochloric acid, which leaves the uranoso-uranic oxide so finely divided that it passes through the filter. (Berzelius.)

B. CARBONATE OF URANIC OXIDE AND POTASH.—*Urano-potassic Carbonate.*—The uranic oxide precipitated by pure potash or its carbonate, dissolves in an aqueous solution of carbonate of potash, but more readily in the bicarbonate, forming a yellow solution, from which the double salt separates in lemon-yellow crystals, or as a crystalline crust. (Chevreul.)—Uranic oxide precipitated by caustic potash is insoluble in monocarbonate of potash, but dissolves completely in bicarbonate, when digested with it; on evaporating the pale yellow solution at a gentle heat, a lemon-yellow crust is obtained, which may be purified by a second crystallization. (Ebelmen.)

	Calculation.		Ebelmen.
2KO	94·4	31·01	31·12
U^2O^3	144·0	47·31	47·13
$3CO^2$	66·0	21·68	21·83
HO			0·40
$2(KO,CO^2) + U^2O^3,CO^2$	304·4	100·00	100·48

At 300°, it gives off carbonic acid, and assumes an orange-yellow colour from formation of uranate of potash. (Ebelmen.) After ignition, it leaves a brick-red mixture of uranate and carbonate of potash. (Berzelius.)

$$2[2(KO,CO^2) + (U^2O^3,CO^2)] = 3(KO,CO^2) + KO,2U^2O^3 + 3CO^2.$$

Dissolves without decomposition in 13·5 parts of water at 15°, and in a smaller quantity of hot water, forming a lemon-yellow solution.—A solution of one part of the salt in 333 parts of water still exhibits a deep yellow colour; in 1332 parts, a pale yellow; in 2664 parts, still paler; in 5328 parts, a mere tinge of yellow; and with 10,656 parts, it is colourless; the latter solution however is rendered turbid by potash, and after a few hours deposits orange-yellow flakes of uranate of potash.

Boiling water, when quite free from potash, dissolves the salt with partial decomposition, and separation of uranate of potash; the latter compound is also deposited after some time from a cold solution when very dilute and not containing an excess of carbonate of potash. Caustic potash precipitates the whole of the uranic oxide from the solution, in the form of uranate of potash, even if a large excess of carbonate of potash is present. Acids if not added in excess, produce the same light yellow precipitate as is produced by carbonate of potash in a salt of uranic oxide. The double salt is perfectly insoluble in alcohol. (Ebelmen.)

C. SULPHATE OF URANOUS OXIDE AND POTASH.—*Uranoso-potassic Sulphate.*—A solution of sulphate of potash and sulphate of uranous oxide yields, when spontaneously evaporated, a green crystalline crust, which is difficultly soluble in water, and at a temperature below redness, evolves sulphuric and sulphurous acids, and leaves the uranium in a higher state of oxidation. (Rammelsberg.)

	Calculation.		Rammelsberg.
KO	47·2	15·12	15·29
2UO	136·0	43·56	44·21
$3SO^3$	120·0	38·44	
HO	9·0	2·88	
$KO,SO^3+2(UO,SO^3)+Aq$	312·2	100·00	

D. SULPHATE OF URANOSO-URANIC OXIDE AND POTASH.—Greyish-green powder which is nearly or quite insoluble in water. (Berzelius.)

E. SULPHATE OF URANIC OXIDE AND POTASH.—*Urano-potassic Sulphate.*—An aqueous mixture of sulphate of uranic oxide and sulphate of potash is evaporated to the crystallizing point, and the double salt purified by re-crystallization. (Arfvedson.) Lemon-yellow, crystalline, granular salt. (Arfvedson.) Not octohedral. (Berzelius.) Forms warty crystalline masses. (Peligot.) Crystalline crust, permanent in the air. (Ebelmen.)

				Berzelius.	
	Crystallized.		Ebelmen.	*a.*	*b.*
KO	47·2	16·32	16·64	15·833	14·60
U^2O^3	144·0	49·80	48·90	52·833	50·84
$2SO^3$	80·0	27·66	27·77	27·834	28·20
2HO	18·0	6·22	6·52	3·500	6·50
$KO,SO^3+U^2O^3,SO^3+2Aq.$	289·2	100·00	99·83	100·000	100·14

The salt *b* examined by Berzelius was crystallized from a solution containing excess of acid. Arfvedson found in the anhydrous salt 13·26 per cent. of potash, 58·06 of uranic oxide, and 28·68 of sulphuric acid.—Alcohol removes from this salt one-fifth of the uranic sulphate (Berzelius.)

The crystallized salt gives off its water when heated (at 120° entirely, *Ebelmen*) and fuses completely at a red heat; on cooling, it appears greenish yellow, but is very little decomposed (according to Ebelmen, not at all): it likewise redissolves in water, forming a pure yellow solution. (Berzelius.) This salt dissolves in 9 parts of water at 22°, and in 5·1 parts of boiling water. Ammonia or hydrosulphate of ammonia added to the solution throws down uranic oxide still containing potash. (Ebelmen.) Alcohol does not dissolve the double salt, and precipitates it from an aqueous solution. (Berzelius.)

F. CHLORIDE OF URANOUS OXIDE AND POTASSIUM.—Called *Chloride of Uranyl and Potassium* by Peligot (who first demonstrated the existence of oxygen in this compound).—By heating the hydrated crystals (*vid. infra*) to a temperature somewhat above 100°, the anhydrous compound is obtained.—The latter fuses at an incipient red heat. (Arfvedson.) When heated with potassium, it is resolved with vivid incandescence into uranous oxide and chloride of potassium. (Berzelius.) When ignited in hydrogen gas, it swells up, and is converted, with formation of hydrochloric acid, into a dark opaque mass. It is not however completely decomposed, even after being submitted to the action of hydrogen for many hours, so that water, though it leaves uranous oxide, nevertheless dissolves out a tolerably large quantity of protochloride of uranium together with the chloride of potassium. When heated above the fusing point, it is partially decomposed, turning green and evolving chlorine. (Arfvedson.) When strongly ignited, it leaves fused chloride of potassium, in which brilliant crystalline scales of uranous oxide are seen to float. (Peligot.)

$$KCl + 2UO,Cl = KCl + 2UO \div Cl.$$

Hydrated Chloride of Uranous Oxide and Potassium, or *Hydrochlorate of Uranic Oxide and Potash.*—An aqueous mixture of sesqui-chloride of uranium and excess of chloride of potassium is evaporated to the crystallizing point.—If the latter does not predominate, the double salt crystallizes with difficulty; as however the double salt and chloride of potassium crystallize with about equal facility, the two kinds of crystals must be picked out one from the other. (Arfvedson.) Peligot recommends the addition of a large excess of hydrochloric acid to the mixture, previous to evaporation. The double salt crystallizes in lemon-yellow, oblique four-sided prisms and rhombic tables. Crystalline system, the doubly oblique prismatic. *Fig.* 129, without the *u*-, *v*-, and *z*-faces; $y : q = 119° 45'$; $y : d = 124° 30'$; $y : e = 133° 5'$; $d : k$ below $= 136° 30'$; $e : s$ below $= 143°$, &c. (Prevostaye, *N. Ann. Chim. Phys.* 6, 165.) Parts with its water a little above 100°. Dissolves very readily in water; but the solution, when evaporated, yields crystals of chloride of potassium, while sesquichloride of uranium remains dissolved. (Peligot.)

	Crystallized.		Peligot.
K	39·2	14·85	13·95
2UO	136·0	51·51	50·47
2Cl	70·8	26·82	26·75
2HO	18·0	6·82	7·30
$KCl,U^2O^2Cl + 2Aq.$	264·0	100·00	98·47

$= KO,HCl + U^2O^3,HCl$. Arfvedson found that the crystals contained: potash 17·37, uranic oxide 35·65, hypothetical anhydrous muriatic acid 20·50, and water 6·49 per cent.

URANIUM AND SODIUM.

A. **URANATE OF SODA.**—Remains on igniting the double acetate of uranic oxide and soda. Colour, pure yellow. Contains one atom of soda with 2 atoms of uranic oxide. (Wertheim.)

B. **CARBONATE OF URANIC OXIDE AND SODA.**—*Urano-sodic Carbonate.*—The uranic oxide precipitated by carbonate of soda dissolves in an excess of the soda-salt, forming a yellow solution. By evaporating a solution of uranate of soda in a warm aqueous solution of bicarbonate of soda, Ebelmen obtained a crystalline crust.

Uranoso-uranic or uranic oxide does not dissolve in carbonate of soda before the blowpipe on charcoal, but imparts to a large quantity of the carbonate—inasmuch as uranate of soda is formed and diffuses itself through it—a yellowish-brown colour (which remains even in the reducing flame). If too large a quantity of the alkaline carbonate is used, the oxide sinks into the pores of the charcoal, without undergoing reduction. (Berzelius.)

C. With borax in the inner flame, uranic oxide is reduced to uranous oxide, yielding a dull green glass, which, if it contains a sufficient quantity of the protoxide, is blackened by gentle flaming; in the outer flame on platinum, a dark yellow glass is obtained. (Berzelius.)

D. ¶ PYROPHOSPHATE OF URANIC OXIDE AND SODA. Prepared by Persoz (*Ann. Pharm.*, 65, 163).—This salt has a pure yellow colour, and is very soluble. The solution may be evaporated to the consistence of a thick gum without crystallizing. It is not decomposed by hydrosulphuric acid or hydrosulphate of ammonia. ¶

E. With microcosmic salt in the inner flame, a beautiful green glass is obtained, especially after cooling; in the outer flame, on platinum, a glass which is yellow while hot, and becomes pale greenish-yellow on cooling. (Berzelius.)

URANIUM AND BARIUM.

URANATE OF BARYTA.—1. Formed when a boiling solution of sesquichloride of uranium and chloride of barium in excess is treated with excess of ammonia; the precipitate rapidly washed on a filter with boiling water, before any carbonate of baryta becomes mixed with it; and lastly dried and ignited. (Arfvedson.) In this process, uranate of ammonia is also precipitated, together with the uranate of baryta. (Berzelius.)—2. By mixing nitrate (or acetate, *Wertheim,*) of uranic oxide with excess of baryta-water, and exhausting the precipitate with water as long as baryta is dissolved. (Berzelius.)—3. By igniting the double acetate of uranic oxide and baryta. (Wertheim.)—4. By boiling nitrate of uranic oxide with a large excess of baryta-water. (Kühn, *Ann. Pharm.* 41, 337.) Uranate of baryta is yellowish-red, or, when reduced to powder, orange-yellow. When it is heated to redness in hydrogen gas, it forms water, and is converted into a mixture of uranous oxide and baryta, spontaneously inflammable at ordinary temperatures. (Berzelius.)

	Calculation.		Berzelius (2).	Wertheim (2or3).	Kühn (4).
BaO	76·6	21·01	21·19	21·43	31·6
$2U^2O^3$	288·0	78·99	78·81	77·89	
$BaO,2U^2O^3$	364·6	100·00	100·00	99·32	

Kühn regards the compound (4) as BaO,U^2O^3; for this, however, the quantity of baryta is insufficient.

URANIUM AND CALCIUM.

A. URANATE OF LIME.—Uranic oxide precipitated by ammonia from an acid solution containing lime, enters into combination with a portion of the lime. (Bucholz.)—Many of the compact, dark yellow varieties of uranium-ochre which, when ignited, remain yellow and yield water but no oxygen gas, likewise contain lime and oxide of lead. (Berzelius.)

¶ B. CARBONATE OF URANIC OXIDE AND LIME.—*Urano-calcic Carbonate.*—Found native as *Liebigite.* (*Vid. Medjidite, infra.*)—This mineral occurs in apparently amorphous, rounded masses, having a distinct cleavage-plane in one direction. It is transparent, has a beautiful apple-green colour and vitreous fracture; hardness between 2 and 2·5. When gently heated, it loses water and becomes greenish grey. Does not fuse at a red heat, but turns black, and acquires an orange-red colour on cooling. With borax it forms a yellowish glass in the outer, and a green glass in the inner flame. Dissolves in dilute hydrochloric acid, with violent effervescence, forming a yellow solution which is precipitated yellow by ammonia and carbonate of ammonia.

	Liebigite.		Smith.
U^2O^3	144	36·3	38·0
CaO	28	7·1	8·0
$2CO^2$	44	11·1	10·2
20HO	180	45·5	45·2
$U^2O^3,CO^2+CaO,CO^2+20Aq.$	396	100·0	101·4

(J. L. Smith, *Ann. Pharm.* 66, 253.) ¶

C. PHOSPHATE OF URANIC OXIDE AND LIME.—*Urano-calcic Phosphate.* Found native in *Calcareous Uran-mica* or *Calcareous Uranite.* Crystalline system, the square prismatic. (*Fig.* 23, 24, 26, 28, 32, 33.) Cleavage distinct, parallel to *p*; less distinct, parallel to *r*. Sp. gr. = 3·1. Hardness equal to that of rock-salt. Lemon-yellow and transparent. When heated it gives off water and becomes straw-coloured and opaque. Before the blowpipe on charcoal it fuses, increasing slightly in bulk, and forms a black mass having a semi-crystalline surface. With carbonate of soda it forms a yellow infusible slag; with microcosmic salt, it gives the usual reactions of uranium. It is soluble in nitric acid. (Berzelius.)

	At.	*Uran-mica*, from Autun.		Peligot.	Berzelius.	Werther.
BaO					1·51	1·03
CaO	1	28·0	6·10	6·20	5·66	5·86
U^2O^3	2	288·0	62·69	63·01	59·37	63·28
cPO^5	1	71·4	15·54	15·20	14·63	14·00
HO	8	72·0	15·67	15·30	14·90	14·30
MgO & MnO					0·19	
F,NH^3 & SnO^2					trace	
Matrix					2·70	
$(CaO,2U^2O^3)cPO^5+8Aq.$		459·4	100·00	99·71	98·96	98·47

¶ D. SULPHATE OF URANIC OXIDE AND LIME.—*Urano-calcic Sulphate.* $U^2O^3,SO^3+CaO,SO^3+15HO$.—A mineral found in conjunction with Liebigite, and accompanying an impure variety of pitchblende obtained from the neighbourhood of Adrianople, appears to have this composition. It is called *Medjidite.*—Transparent; of dark copper-yellow colour and imperfectly crystalline texture; fracture horny. Hardness about 2·5. At a gentle heat it loses water and assumes a lemon-yellow colour; blackens at a red heat. With borax in the blowpipe flame it behaves like *Liebigite.* Insoluble in water, but dissolves sparingly in dilute hydrochloric acid. (Smith.) ¶

	Medjidite.	
U^2O^3	144	37·21
CaO	28	7·24
$2SO^3$	80	20·67
15HO	135	34·88
$U^2O^3,SO^3+CaO,SO^3+15Aq.$	387	100·00

URANIUM AND MAGNESIUM.

URANATE OF MAGNESIA.—Prepared by igniting the double acetate of uranic oxide and magnesia. Yellowish brown. Its formula is MgO, $2U^2O^3$. (Wertheim.)—The precipitate which ammonia produces in a mixture of nitrate of uranic oxide and nitrate of magnesia, contains magnesia and ammonia besides uranic oxide. (Berzelius.)

URANIUM AND SILICIUM.

Hydrated Fluoride of Silicium and Uranium, or *Hydrofluate of Silica and Uranous Oxide.*—Hydrofluosilicic acid gives with protochloride of uranium a pale green gelatinous precipitate. If an excess of hydrofluosilicic acid is present, the solution retains a bluish green colour. The precipitate, heated out of contact of air, yields water, hydrofluoric acid, and sublimed silica. It is but slightly changed by boiling with solution of potash. After drying it dissolves very sparingly in acids. (Rammelsberg.)

Uranic oxide imparts to glass-fluxes a yellow colour with a greenish cast.

URANIUM AND TANTALUM.

Uranotantalite appears to consist of *Tantalate of Uranous oxide.* (G. Rose, *Pogg.* 48, 555.)

URANIUM AND TUNGSTEN.

A. TUNGSTATE OF URANOUS OXIDE, or URANOUS TUNGSTATE.—Bitungstate of ammonia gives a brown precipitate with protochloride of uranium.—The pale green solution still contains tungstic acid, together with a small quantity of uranic oxide.—Boiling potash removes the whole of the tungstic acid from the moist precipitate, but only a part after drying; ammonia separates a portion only, even from the moist precipitate; carbonate of soda, in a state of fusion, decomposes it entirely. Nitric acid dissolves the uranous oxide contained in the salt, converting it into uranic oxide, and leaves insoluble yellow tungstic acid, which however retains a portion of the uranic oxide. The salt, when treated with hydrochloric acid, turns blue and dissolves, forming a green solution, from which alkalis precipitate uranoso-uranic oxide. It is insoluble in oil of vitriol. (Rammelsberg.)

	Calculation.		Rammelsberg.
2UO	136	24·73	25·88
$3WO^3$	360	65·45	64·84
6HO	54	9·82	9·25
$2UO,3WO^3 + 6Aq.$	550	100·00	99·97

B. TUNGSTATE OF URANIC OXIDE, or URANIC TUNGSTATE.—Light yellow salt, insoluble in water, but soluble in the stronger acids and in carbonate of ammonia. (Berzelius.)

URANIUM AND MOLYBDENUM.

A. MOLYBDATE OF URANOUS OXIDE, or URANOUS MOLYBDATE.—An excess of hydrochlorate of uranous oxide forms a greenish black precipitate with monomolybdate of ammonia. The supernatant liquid appears dark blue, because a portion of the uranous oxide and a portion of the molybdic acid decompose each other, yielding uranic oxide which remains dissolved, and blue oxide of molybdenum. If an additional quantity of ammonia be then added to the solution, a dark blue precipitate separates, which is a mixture of blue oxide of molybdenum and molybdate of uranic oxide.—The greenish black precipitate, freed by long-continued washing with hot water from the blue oxide of molybdenum, leaves a brownish powder, consisting of molybdate of uranous oxide mixed with a small quantity of molybdate of uranic oxide. When ignited, it loses 9·07 per cent. of water, and fuses to a yellowish green crystalline mass, a portion of the molybdic acid being at the same time sublimed. It likewise contains 39·5 per cent. of uranous oxide. Boiling potash separates the molybdic acid from the powder, and leaves dark-coloured protoxide of uranium containing a portion of sesquioxide. Hydrochloric acid dissolves the powder, forming a green solution, which becomes yellow when diluted.—If protochloride of uranium is precipitated by an excess of molybdate of ammonia, a scanty, brownish precipitate is formed, which rapidly becomes dark green, and, on the application of heat, dissolves in the dark green supernatant liquid. (Rammelsberg.)

B. MOLYBDATE OF URANIC OXIDE, or URANIC MOLYBDATE.—Molybdate of ammonia precipitates from sulphate of uranic oxide a pale sulphur-yellow powder, which contains 56·25 per cent. of uranic oxide, and 43·75 of molybdic acid. The precipitate turns blue, either when brought in contact with moist paper, or by long exposure to heat (Brandes); it is insoluble in water, but dissolves in the stronger acids, and in carbonate of ammonia. (Berzelius.)

C. URANIC SULPHOMOLYBDATE.—A compound of tersulphide of molybdenum with sesquisulphide of uranium.—Formed when a salt of uranic oxide is precipitated by sulphomolybdate of potassium.—The precipitate is dark brown, and permanent in the air. (Berzelius.)

D. URANIC PERSULPHOMOLYBDATE.—A compound of tetrasulphide of molybdenum with sesquisulphide of uranium.—An aqueous solution of persulphomolybdate of potassium added to the solution of a uranic salt, throws down a dark red powder. (Berzelius.)

URANIUM AND VANADIUM.

VANADIATE OF URANIC OXIDE, or URANIC VANADIATE.—Uranic salts give lemon-yellow precipitates both with monovanadiate and with bivanadiate of potash. (Berzelius.)

URANIUM AND CHROMIUM.

Protochloride of uranium yields with monochromate of potash, a yellowish brown precipitate, which is soluble in excess of protochloride of uranium, and appears to be a mixture of chromate of uranic oxide, and chromite of uranous oxide. (Rammelsberg.)

CHROMATE OF URANIC OXIDE, or URANIC CHROMATE.—*a. More neutral salt?*—Monochromate of potash gives an ochre-yellow precipitate with nitrate of uranic oxide. (Moser.)

b. Acid chromate?—The yellow rough-flavoured solution of uranic carbonate in aqueous chromic acid yields small, bright red, cubic and dendritic crystals. The salt fuses at a low red heat, undergoing partial decomposition: on dissolving the dark brown mass in water, small portions of chromic oxide and uranoso-uranic oxide remain behind. (John.)

OTHER COMPOUNDS OF URANIUM.

When hydrogen gas is passed over the compounds of uranic oxide with the oxides of lead, iron, copper, &c., heated to redness, residues are obtained which take fire in the air at ordinary temperatures, and are reconverted into uranates of the metallic oxides. (Arfvedson.)—The conclusion of Arfvedson that alloys of uranium with the above metals are produced under these circumstances, is rendered doubtful by Peligot's researches; probably they are mere mixtures of lead, iron, or copper, with uranous oxide; since, according to Peligot, these compounds are likewise pyrophoric.

CHAPTER XXIII.

MANGANESE.

Scheele. *Opusc.* 1, 227; also, *Crell. N. Entd.* 1, 112 & 140.
Hjelm. *Crell. Ann.* 1787, 1, 158 & 446.
Bergman. *Opusc.* 2, 201.
John. *N. Gehl.* 3, 452; 4, 436.
Berzelius. Oxides of Manganese. *Schw.* 7, 76.—Also, *Ann. Chim. Phys.* 5, 149; also, *N. Tr.* 2, 2, 359.
Berzelius & Arfvedson. *Ann. Chim. Phys.* 6, 204.
Arfvedson. Oxides of Manganese. *Schw.* 42, 202.—Sulphide of Manganese, *Pogg.* 1, 50.

Chevreul. Mineral Chameleon. *Ann. Chim. Phys.* 4, 42; also, *Schw.* 20, 324; also, *N. Tr.* 2, 1, 188.

Chevillot & Edwards. Mineral Chameleon. *Ann. Chim. Phys.* 4, 287; 8, 337; also, *N. Tr.* 2, 1,199; 3, 2, 113; the former also in *Schw.* 20, 332.

Berthier. Oxides of Manganese. *Ann. Chim. Phys.* 20, 187.

Forchhammer. Manganic and Permanganic Acids. *Ann. Phil.* 16, 130; also, *N. Tr.* 6, 1, 277. Oxides and Salts of Manganese. *Ann. Phil.* 17, 50.

Fromherz. Permanganic Acid. *Schw.* 41, 257; also, *Pogg.* 31, 677.——Salts of Manganese. *Schw.* 44, 327.

Turner. Oxides of Manganese. *Edinb. J. of Sc.* 4; also, *Phil. Mag. Ann.* 4, 22 and 96; also, *Kastn. Arch.* 14, 359 and 424; further, *Schw.* 56, 166; *Pogg.* 14, 211.

Brandes. Salts of Manganese. *Pogg.* 20, 556.

Mitscherlich. Manganic and Permanganic Acids. *Pogg.* 25, 287; also, *Schw.* 65, 62.

Bachmann. *Zeitschr. Phys. Math.* 4, 312; 6, 172; also, *Schw.* 55, 72; *Zeitschr. Phys. v. W.* 1, 262.

Schönbein. Manganic and Permanganic Acids. *J. pr. Chem.* 41, 225.

Heintz. Manganous Salts. *Pogg.* 71, 449.

Völker. *Ann. Pharm.* 59, 35.

Mangan, Braunstein-metal, Magnesium, Mánganum, Manganèse.

History.—Black oxide of manganese, a substance long used to decolorize glass, and called *Magnesia nigra* from its resemblance to the loadstone, was formerly included among the ores of iron. It was, however, proved by the researches of Pott, in 1740, of Kaim and Winterl, in 1770, and of Scheele and Bergmann, in 1774, that the metal contained in this mineral is distinct from iron, and possesses characters peculiar to itself. The metal itself was first eliminated by Gahn.—Chevillot & Edwards, in 1818, pointed out that *Mineral Chameleon*, a substance discovered some considerable time before, contained a peculiar acid of manganese.—Forchhammer, in 1820, distinguished two acids of manganese; and Mitscherlich, in 1832, fully confirmed the distinction.

Sources. This metal occurs in the several forms of manganoso-manganic oxide; manganic oxide; hydrated manganic oxide; peroxide; hydrated peroxide; sulphide of manganese; carbonate of manganous oxide; silicate of manganous oxide; double silicate of alumina and manganous oxide; a compound of manganic oxide and baryta; titanate of manganous oxide; a compound of manganic oxide and cupric oxide; in Helvin; and in Earthy Cobalt. Also, in small quantities, often as colouring matter, in a great number of siliceous minerals; in very small quantity in plants; and in still smaller quantity in animal substances.

Preparation.—1. Either of the pure oxides of manganese is moistened several times with oil, and heated to redness; then made into a thick paste with a small quantity of oil; introduced into a charcoal crucible (III., 467); covered with charcoal powder; and exposed to the strongest heat of a powerful blast-furnace. (John.)—2. An oxide of manganese is mixed with a quantity of lamp-black, much less than that which is required to reduce it, and the mixture made into a pasty mass with oil; it is then pressed into a charcoal crucible covered with charcoal powder; and the bottom of a crucible fitted tight into the opening, and luted on with clay; the whole is then heated in a blast-furnace for an hour.—3. According to Pfaff, peroxide of manganese yields a metallic bead before the oxy-hydrogen blow-pipe. The manganese obtained by the first and second methods contains carbon (from 0·1 to 2·9 per cent., together with 1·9 per cent. of silicium, [from the charcoal,] *Bachmann*). On fusing it with borax, the carbon is separated (according to John), and the metal becomes more fusible; under these circumstances, however, it may combine with boron or sodium. The metal is preserved in an inverted vessel filled with mercury, or under rock-oil, or in a sealed glass tube.

Properties.—Greyish white, without much metallic lustre; very soft, very brittle, and very easily split; has a fine granular texture; specific gravity = 6·85, (Bergmann,) 7·0 (Hjelm), 8·013 (John). Fuses in the strongest heat of a blast-furnace.

¶ According to Berzelius, manganese, like silicium and many other elements, is susceptible of two allotropic conditions. As obtained by reduction with carbon in the blast-furnace, it has the well known property of oxidizing at ordinary temperatures, either in the air or under water, with evolution of hydrogen. Sefström, however, has observed that, when manganese is reduced in contact with silica, (the resulting compound containing about 6 or 7 per cent. of silicium), a regulus is obtained, which does not differ much in appearance from the ordinary variety, though wanting all its usual characters:—for instance, it sustains a red heat without oxidation, and resists the action of aqua-regia. The presence of the silicium is not sufficient to account for this peculiarity, inasmuch as platinum, when alloyed with a large quantity of silicium, is readily dissolved by aqua-regia. It must, therefore, arise from the altered condition of the metal itself; the silicium, in its transformation into Siβ (III., 352), probably induces the change of the manganese into Mnβ, at a temperature at which this change would not take place with manganese alone. This peculiar condition of manganese may explain the peculiarities of the native red siliceous manganese, and of many other silicates containing manganese, which are perfectly indifferent to acids, even to nitric acid, which usually raises lower oxides to higher degrees of oxidation. ¶

Atomic weight = 27·6 Berzelius; 28 (Turner).

Compounds of Manganese.

MANGANESE AND OXYGEN.

Among the heavy metals, manganese, iron, and zinc, have the greatest affinity for oxygen; and at ordinary temperatures, none of them are oxidized so rapidly as manganese, either in the air or under water. It is oxidized still more rapidly by all the aqueous acids, the action being attended either with evolution of hydrogen gas having a peculiarly offensive odour, or, as in the case of nitric acid, with decomposition of the acid.

Manganese kept under water and out of contact of air, as long as it disengages hydrogen gas, is converted into a green oxide, in which 100 parts of manganese are combined with only 14·9 parts of oxygen. (John.) Similar results were obtained by Bachmann:—the manganese was very slowly disintegrated in cold water, but more rapidly in hot water; hydrogen gas, having a fœtid odour, being evolved, and a greyish white oxide produced, which, when ignited out of contact of air, became greenish grey, and pale green on cooling; in an earlier experiment, 100 parts of metal had absorbed in this process 14·285 parts of oxygen (=28:4); according to a later experiment, the amount of oxygen was 19·5 (=28 : 5·46). Hence, the oxide formed by the action of water appears to be a suboxide; according to Bachmann, however, it dissolved in hydrochloric acid without disengagement of hydrogen gas, and formed protochloride of manganese.

From these experiments, it might be concluded, that what has hitherto been regarded as metallic manganese really contains oxygen; and hence, in passing to the state of manganous oxide, it takes up less oxygen than is commonly supposed. The statements of John and Bachmann, however, require confirmation. According to Regnault (*Ann. Chim. Phys.* 62, 350), finely divided manganese, kept under water at ordinary temperatures, slowly liberates hydrogen gas; but if heat be applied even much below 100°, the evolution of gas becomes rapid, and the manganese is converted into a yellowish brown powder, which becomes dark brown on exposure to the air.

The hydrogen gas, obtained by dissolving manganese in dilute sulphuric acid, deposits, when exploded with an excess of oxygen gas, a white, greasy substance, which retains the disagreeable odour of the gas. Manganese, gently heated in a current of oxygen gas, becomes red-hot from the heat evolved by its combustion. Carbonic oxide gas does not appear to be decomposed by manganese at a red heat. (Bachmann.) Manganese does not reduce any simple metallic salt, except the salts of silver and gold; and with these the reduction is very slight. (Fischer, *Pogg.* 16, 128.)

A. MANGANOUS OXIDE. MnO.

Protoxide of Manganese, Manganoxydul.

Formation.—By exposing manganese to the action of water, air being excluded; by dissolving manganese in any aqueous acid; often also by the action of an acid on the higher oxides of manganese.

Preparation.—1. By gently igniting carbonate of manganous oxide (or the hydrated oxide: *H. Davy*) in a vessel from which the air is excluded (Scheele); or by passing hydrogen gas over the salt during ignition, to prevent any oxidation from without. (Arfvedson.)—2. By passing hydrogen over gently ignited manganoso-manganic oxide. (Forchhammer, Turner; see also Fuchs, *Schw.* 60, 345.)—3. By exposing manganoso-manganic oxide, manganic oxide, or peroxide of manganese, for a long time to a moderate white heat in a charcoal crucible. (Berthier.)—4. By igniting oxalate of manganous oxide out of contact of air. (Lassaigne.)—5. By mixing equal parts of fused chloride of manganese and carbonate of soda with a small quantity of sal-ammoniac, heating the mixture till it fuses, and exhausting the fused mass with water, when cold. (Liebig & Wöhler, *Pogg.* 21, 584.)—6. By igniting oxalate of manganous oxide in a retort. (Bachmann.)—Manganous oxide is pale

green (Forchhammer), pistachio-nut green (Arfvedson), tincal-green (Turner), dark greyish green (Berzelius), greenish grey (Liebig & Wöhler), sometimes pale greyish green, sometimes pale green (Gmelin), greenish black, (H. Davy); turns pale yellow when heated (Forchhammer). Pulverulent after gentle ignition; cakes together when more strongly heated. According to Despretz (*Ann. Chim. Phys.* 43, 322), it fuses in the blast-furnace, and forms a mass having a fine green colour.

	Calculation.		Forchhammer.		Berzelius & Arfvedson.	H. Davy.	Bergman.
Mn	28	77·78	76·16	to 76·78	78·07	79	80
O	8	22·22	23·84	,, 23·22	21·93	21	20
MnO	36	100·00	100·00	100·00	100·00	100	100

(MnO = 345·89 + 100 = 445·89. Berzelius.)

Decompositions.—When ignited alone, it does not part with oxygen at any temperature; at a bright red heat, it is decomposed by charcoal, but not by hydrogen or carbonic oxide gas. When ignited in a current of sulphuretted hydrogen gas, it is resolved into water and 123·66 per cent. of sulphide of manganese; and by ignition with sulphur, into sulphurous acid and oxysulphide of manganese. (Arfvedson.)

Combinations.—*a.* With Water.—Hydrated Manganous Oxide.—Prepared by decomposing a soluble salt of manganous oxide with potash. —White flocculent precipitate.—According to Sir H. Davy, it contains 24 per cent. of water.—When exposed to the air, it rapidly turns brown, from formation of hydrated manganic oxide, or, according to Phillips, of hydrated peroxide of manganese.

b. With Acids, forming the Salts of Manganous Oxide, or Manganous Salts. The protoxide has a great affinity for acids, and its salts are very nearly neutral to test-paper. They are for the most part soluble in water, and either pale rose-coloured or colourless.* Those which contain a fixed acid, sustain a strong red heat without decomposition. With fluxes they behave like the oxides of manganese. (*Vid. Manganese and Sodium.*) Those manganous salts which are insoluble in water, dissolve in hydrochloric acid. Those which are soluble in water have an astringent taste. The protoxide of manganese contained in the solution of one of these salts is not converted into a higher oxide by atmospheric air, nitric acid, or chlorine. The hydrated peroxide is very slowly precipitated from the solutions of these salts by chloride of lime, according to Phillips, and very slowly by hypochlorous acid, according to Balard; likewise by bromic acid, (Rammelsberg,) or bromate of potash on the addition of oil of vitriol, or by chlorate of potash with oil of vitriol, on the application of heat (the addition of a small quantity of chlorate produces only a reddish colour in the solution). (Simon, *Repert.* 65, 208.) Manganese is not precipitated in the metallic state by other metals. Caustic potash and soda

* ¶ Völker (*Ann. Pharm.* 59, 27) has shown that the reddish tint observed in solutions of manganous salts, especially when in large quantity, is owing to the presence of a higher oxide, and that the pure salts are perfectly colourless. In some cases, however, it is caused by a small quantity of cobalt, which usually accompanies manganese; but this may be readily determined by adding sulphurous acid or some organic substance to the solution, whereupon, if the colour proceeds from the presence of a higher oxide, it instantly disappears.¶

separate the whole of the manganese in the form of white hydrate of manganous oxide, which rapidly turns brown in the air. Ammonia, when added even in large excess, precipitates from a neutral solution only half of the manganous oxide, in the form of a white hydrate which turns brown in the air; the remainder of the manganous oxide unites with the ammoniacal salt produced, and forms a double salt not decomposible by ammonia out of contact of air:

$$2(MnO,SO^3) + NH^3 = (NH^3,SO^3 + MnO,SO^3) + MnO.$$

If then the solution contains a quantity of free acid, at least equal to that which is in combination, or if it contains a corresponding quantity of an ammoniacal salt, ammonia produces no precipitate; because the ammoniacal salt—either formed at the time or already present—combines with the salt of manganese, forming a double salt which is not decomposed by ammonia. From the same cause, the hydrated protoxide of manganese precipitated by either of the alkalis, redissolves in sulphate, hydrochlorate, or nitrate of ammonia, with disengagement of free ammonia. Nevertheless such a mixture of a double salt of manganous oxide and ammonia with excess of ammonia gradually becomes turbid in the air; and, if the latter be present in sufficient quantity, deposits the whole of the manganese in the form of brown hydrated sesquioxide. In this case, the affinity of ammonia in excess for the acid combined with the manganous oxide, and that of the atmospheric oxygen for the manganous oxide, act together in producing the result. Monocarbonate of ammonia, potash, or soda throws down white carbonate of manganous oxide, which does not turn brown in the air, and is sparingly soluble in a cold solution of sal-ammoniac. Bicarbonate of potash precipitates a concentrated solution immediately, and renders a dilute solution slightly turbid; but if the latter contains any free acid, so that an excess of carbonic acid is set free, no precipitate is formed. In this case, bicarbonate of manganous oxide is formed, which can exist only in the presence of a large quantity of water; after long exposure to the air, however, white monocarbonate of manganous oxide is precipitated and carbonic acid evolved. Carbonate of lime, even with the aid of heat, gives no precipitate with manganous salts. (Fuchs, *Schw.* 62, 192.) The carbonates of baryta, strontia, lime, and magnesia do not precipitate these salts at ordinary temperatures, but completely on the application of heat. (Demarçay, *Ann. Pharm.* 11, 240.) Carbonate of magnesia precipitates the manganese completely on boiling; calcined magnesia still more quickly. (Döbereiner, *Schw.* 63, 482.) Phosphate of soda throws down white phosphate of manganous oxide which does not undergo any alteration in the air (a precipitate is obtained even with a solution containing one part in 500. *Pfaff*). Hydrosulphuric acid gas or water saturated with it does not affect those salts of manganous oxide which contain one of the stronger acids, such as the sulphuric, hydrochloric, or acetic acid, even when the acid is not in excess: the most that appears is a scanty white turbidity, arising from a trace of hydrated sulphide of manganese, which disappears on the addition of a small quantity of acid. (Wackenroder, *N. Br. Arch.* 16, 114.) But if ammonia is added, or if the solution of the salt is mixed with an alkaline hydrosulphate, the manganese is completely precipitated in the form of flesh-coloured hydrated sulphide of manganese (or hydrosulphate of manganous oxide), which is insoluble in excess of the alkaline hydrosulphate, but dissolves readily in concentrated acetic acid, and turns brownish-black on exposure to the air. If a small quantity of iron be present, the precipitate appears brown or black. Sulphite of potash (but not sulphite of ammonia) added to a manganous salt, throws down sulphite of manganous oxide on boiling. (Berthier.) Arseniate of soda throws down white arseniate of manganous oxide. Oxalic acid precipitates from concentrated (not from dilute) solutions, after some time, a white crystalline powder, consisting of manganous oxalate, soluble in hydrochloric or sulphuric, but not in oxalic acid. Alkaline oxalates produce the same precipitate even in dilute solutions, not however in presence of sal-ammoniac, nor with a large excess of the alkaline oxalate. Ferrocyanide of potassium gives—in a solution containing 1 part of salt in 6000 parts of water (Pfaff)—a white (or if copper is present, a reddish) precipitate which is easily soluble in hydrochloric acid, unless, according to Otto (*Ann. Pharm.* 42, 348), the solution contains an excess of the ferrocyanide, or of sal-ammoniac and other salts. Ferricyanide of potassium gives a brownish-yellow precipitate insoluble in hydrochloric acid.

The following re-agents produce no effect: chromate of potash, alkaline succinates and benzoates, and tincture of galls.

B. MANGANOSO-MANGANIC OXIDE. Mn^3O^4.

Red Oxide of Manganese, Brown Oxide of Manganese, Deutoxyde de Manganèse, Manganoxyd.—Found native as *Hausmannite.*

Formation.—1. Manganese exposed to (moist) air at ordinary temperatures, evolves hydrogen gas of a peculiar odour, and is converted into a reddish brown powder. This must be regarded as a mixture of manganese containing charcoal and silicium, with manganoso-manganic oxide; since it dissolves in hydrochloric acid, with evolution of hydrogen gas, and forms a brown solution, which, when heated, becomes colourless and gives off chlorine. The oxidation takes place more rapidly, in proportion as the manganese is more free from charcoal and the air is warmer and contains more moisture. On dissolving the powder in hydrochloric or nitro-hydrochloric acid, carbide of manganese [graphite?] remains in brilliant scales. (Bachmann.) If the metal is heated in the air, the conversion into manganoso-manganic oxide takes place more rapidly, but without incandescence; in oxygen gas, the finely divided metal becomes ignited. Carbonic acid is produced at the same time from the charcoal present in the manganese. (Bachmann.)—2. The protoxide of manganese obtained by gentle ignition—not the denser variety obtained by previous exposure to a white heat, or prepared by the fourth method—turns brown after exposure to the air for a few days, at ordinary temperatures. If it be heated to a temperature below redness, or brought in contact at one point only with a red-hot coal, it takes fire—as formerly observed by Scheele—and is quickly converted into manganoso-manganic oxide, exhibiting incandescence all the while; the denser variety of manganous oxide, when heated to low redness, absorbs oxygen without incandescence. According to Arfvedson, 100 parts of manganous oxide thus treated yield from 107·04 to 107·35 parts of manganoso-manganic oxide. The protoxide ignited in aqueous vapour is converted, with disengagement of hydrogen gas, into manganoso-manganic oxide. (Regnault.)—3. The higher oxides, when strongly ignited, evolve oxygen, and are reduced to the red oxide.

Preparation.—1. Pure sulphate or hydrochlorate of manganous oxide is prepared from peroxide of manganese (*see these salts*); carbonate of manganous oxide precipitated from it by the addition of an alkaline carbonate; and the precipitate washed and dried in the air, and lastly ignited.—2. Pounded peroxide of manganese is freed from impurities, such as carbonate of lime, by dilute hydrochloric acid; then mixed with four times [this is too much] its weight of oil of vitriol; the liquid evaporated to dryness; the residue dissolved in water; and copper precipitated from the filtrate by hydrosulphuric acid: the excess of the latter is then expelled from the filtered solution by boiling, and manganous carbonate (containing iron) precipitated from the solution by the addition of carbonate of potash. The washed precipitate is then treated with aqueous oxalic acid in excess, which dissolves the iron; and the remaining manganous oxalate is purified with water, and afterwards dried and ignited in the air. (Lassaigne, *Ann. Chim. Phys.* 40, 329; also *Schw.* 56, 160.)

Hausmannite occurs in acute square-based octohedrons. *Figs.* 21 and 22; $e : e' = 105° 25'$; $e : e'' = 117° 54'$; cleavage comparatively easy parallel to *p*; less easy parallel to *e*. Sp. gr. =4·72. Hardness between fluorspar and felspar. Brownish black, with semi-metallic lustre. Yields a brown powder which dissolves in cold concentrated sulphuric acid, forming a red solution. (Haidinger.) The artificial oxide appears sometimes as a reddish brown, sometimes as a cinnamon-coloured powder, which turns black whenever it is heated.

	Calculation.		Arfvedson.	Berzelius & Arfvedson.	Bergman.	Forchhammer.
3Mn	84	72·41	72·77	72·74	74	70·4
4O	32	27·59	27·23	27·26	26	29·6
Mn^3O^4	116	100·00	100·00	100·00	100	100·0

Or:			Arfvedson.	Or:		
MnO	36	31·03	31·068	2MnO	72	62·07
Mn^2O^3	80	68·97	68·932	MnO^2	44	37·93
MnO,Mn^2O^3	116	100·00	100·000	$2MnO,MnO^2$	116	100·00

$$Mn^3O^4 = 3 \,.\, 345{\cdot}89 + 4 \,.\, 100 = 1437{\cdot}67. \quad \text{(Berzelius.)}$$

Turner found in Hausmannite: manganoso-manganic oxide, 98·098 per cent.; excess of oxygen, 0·217; baryta, 0·111; silica, 0·337; water, 0·435; besides traces of a metallic chloride. Rammelsberg found: protoxide of manganese, 92·487; oxygen, 7·004; baryta, 0·150 (loss 0·359).

Decompositions.—1. Reduced to the metallic state by heating to whiteness with charcoal. 100 parts of manganoso-manganic oxide heated in a charcoal crucible yield 73·4 of metallic manganese. (Berthier.)—2. Boiling concentrated nitric acid removes the protoxide from manganoso-manganic oxide, first colouring it brown, and then converting it into black peroxide. (Berthier.) 100 parts of manganoso-manganic oxide, when boiled with dilute nitric acid, yield 47·93 parts of hydrated peroxide. (Forchhammer.)—The peroxide obtained from 100 parts of manganoso-manganic oxide yields on ignition, 35 parts (Berthier), 34·03 parts (Forchhammer) of manganoso-manganic oxide; so that $\frac{2}{3}$ of the manganese contained in the manganoso-manganic oxide is dissolved by the nitric acid in the form of manganous oxide:

$$Mn^3O^4 = 2MnO + MnO^2.$$

116 parts of manganoso-manganic oxide yield with boiling dilute sulphuric acid (containing about 1 part of oil of vitriol to 11 parts of water) a solution of manganous sulphate and 44 parts of peroxide of manganese. (Turner.)—3. Hydrochloric acid heated with maganoso-manganic oxide forms protochloride of manganese and gives off chlorine. Hot oil of vitriol decomposes this oxide, forming sulphate of manganous oxide and liberating oxygen gas. 100 parts of manganoso-manganic oxide fused with bisulphate of potash evolve 7·5658 parts of oxygen. (Forchhammer.)

Combinations.—*a.* With Water:—Hydrate of Manganoso-manganic Oxide.—Prepared by precipitating a salt of manganoso-manganic oxide by solution of potash. Its colour is brown.

b. With Acids:—Forming the Manganoso-manganic salts.—Manganoso-manganic oxide dissolves only in hot and highly concentrated phosphoric oxide, or in cold concentrated sulphuric, hydrochloric, oxalic, or tartaric acid, in small quantity and without neutralizing the acid. The solution in phosphoric or sulphuric acid is bright red; the others dark brown. Heat and the addition of water, or of deoxidizing agents, converts these salts (the phosphate excepted) into salts of manganous oxide with large excess of acid. The manganoso-manganic salts should perhaps be regarded merely as mixtures of manganous and manganic salts; manganic oxide, however, does not appear to be soluble in acids by itself.

C. Manganic Oxide. Mn^2O^3.

Sesquioxide of Manganese, Black Oxide of Manganese, Tritoxyde de Manganèse, Manganoxyd.

Found native in the form of *Braunite.*—*Formation and Preparation.* —1. By exposing peroxide of manganese or nitrate of manganous oxide to a dull red heat for a considerable time.—2. Probably also by prolonged and very gentle ignition of metallic manganese, manganous oxide, or manganoso-manganic oxide, in open vessels.—3. Probably also in some of the decompositions of manganoso-manganic oxide by acids.

Braunite forms acute square-based octohedrons. *Figs.* 21, 24, and other forms. $e : e' = 109° 53'$; $e : e'' = 108° 39'$. Cleavage parallel to *p*. Sp. gr. = 4·82. Hardness equal to that of felspar. Lustre semi-metallic. Colour, brownish-black. Yields a powder of the same colour. (Haidinger.) Artificially prepared manganic oxide is a black powder.

	Calculation.		Berzelius & Arfvedson.	Forchhammer.	Arfvedson.	John.	H. Davy.
2Mn	56	70	70·35	70·4	70·76	71·33	71·43
3O	24	30	29·65	29·6	29·24	28·67	28·57
Mn^2O^3	80	100	100·00	100·0	100·00	100·00	100·00

Or:

MnO	36	45
MnO^2	44	55
MnO,MnO^2	80	100

Or:

			Turner. *Braunite.*
2MnO	72	90	86·94
O	8	10	9·85
BaO			2·62
SiO^2			trace
HO			0·95
	80	100	100·36

$Mn^2O^3 = 2 . 345·89 + 3 . 100 = 991·78$. (Berzelius.)

Decompositions.—1. When strongly ignited, it disengages oxygen gas and is converted into manganoso-manganic oxide. The loss of oxygen amounts to 3·05 per cent. (Forchhammer.)—2. Decomposed by boiling with nitric acid, into protoxide of manganese which dissolves, and peroxide which remains undissolved. (Berthier.) The same result is obtained when manganic oxide is boiled with dilute sulphuric acid. (Turner.)—3. Hot oil of vitriol reduces it to manganous oxide and dissolves it, with evolution of oxygen gas; in hot hydrochloric acid it dissolves with evolution of chlorine.

Combinations.—*a.* With Water.—HYDRATED MANGANIC OXIDE.—Found native as *Manganite* or *Manganese-glance.*—Obtained: 1. By exposing the hydrated protoxide to the action of the air.—2. According to Berthier, by passing chlorine gas through water in which carbonate of manganous oxide is diffused, the chlorine not being in excess. The liquid is filtered, and the undecomposed carbonate removed by cold dilute nitric or acetic acid. A portion of hydrated peroxide, however, remains mixed with the hydrated sesquioxide.

The native compound forms large, steel-grey, rhombic prisms, belonging to the right prismatic system. *Fig.* 61 and other forms. $u : u^1 = 99° 40'$; cleavage parallel to u, u', m and t; less distinct parallel to p.—Specific gravity 4·328; hardness equal to that of felspar. (Haidinger.) Yields a reddish brown powder, which does not impart any colour, or only a slight tinge of red, to cold concentrated sulphuric acid. The artificially prepared hydrate is a bulky, dark brown powder, consisting of minute scales; does not decrease in volume when heated in the water-bath; it leaves a stain when rubbed.—Resolved by boiling with moderately concentrated sulphuric acid, into protoxide of manganese which dissolves, and hydrated peroxide which remains undissolved. (Berthier.)

	Calculation.		Or:			Turner. Ilefeld.
2Mn	56	62·92	2MnO	72	80·90	80·92
3O	24	26·97	O	8	8·99	8·98
HO	9	10·11	HO	9	10·11	10·10
Mn^2O^3,Aq.	89	100·00		89	100·00	100·00

Or:			Arfvedson. Undenäs.	Berzelius & Arfvedson. Undenäs.	Turner. Ilefeld.
$2Mn^3O^4$	232	86·89	86·41	86·93	86·85
O	8	3·00	3·51	3·07	3·05
3HO	27	10·11	10·08	10·00	10·10
$3(Mn^2O^3 + Aq.)$	267	100·00	100·00	100·00	100·00

b. By the intervention of other salifiable bases, manganic oxide may be made to unite with certain acids, forming bright red, very soluble compounds—MANGANIC SALTS—from which, according to Fuchs, carbonate of lime precipitates the manganic oxide.

Ores of manganese, containing more than 1½ and less than 2 atoms of oxygen to 1 atom of manganese.

1. *Compact and Fibrous Manganese ore, Psilomelane, Hartmangan, Schwarzer Glaskopf, Schwarzeisenstein.*—Amorphous, dense, or stalactitic. Specific gravity from 4·08 to 4·36; harder than apatite; fracture conchoidal; black.—It is probably $MnO,2MnO^2$; but the MnO is often

partly replaced by KO, BaO, CaO, CuO, &c. Water also is often present, and sometimes the proportion of MnO^2 is greater; but the amorphous state of the mineral renders it impossible to determine whether this additional quantity of MnO^2 is an essential constituent, or merely an accidental admixture. In *Earthy cobalt* and *Cupreous manganese* the MnO is entirely replaced by CoO and CuO. (See these minerals.) Many varieties of Psilomelane likewise contain carbonic acid, so that when ignited, they evolve that gas at first instead of oxygen.

	Wackenroder.	Fuchs.	Rammelsberg.	Turner.	
	a.	*b.*	*c.*	*d.*	*e.*
KO		4·5	3·05		
NaO		trace	0·32		
BaO	1·1			16·365	16·69
CaO			0·38		
CuO			0·96		
Mn^3O^4	84·9	81·8	81·36	69·795	70·97
O	6·0	9·5	9·18	7·364	7·26
Fe^2O^3	4·5		1·43		
SiO^2	1·0	trace	0·54	0·260	0·95
HO	2·5	4·2	3·39	6·216	4·13
	100·0	100·0	100·61	100·000	100·00

a is from Ilmenau; *b* from Baireuth; before ignition it gives up none of its potash to boiling water, but after ignition the whole;—*c* from Horhausen; *d* from Schneeberg; *e* from Romanèche. If the sesquioxide of iron and silica are regarded as adventitious, calculation gives nearly the following formulæ: $a = MnO, 2MnO^2$; $b = KO, 3MnO, 20MnO^2 + 4Aq. = 1$ Base : $5MnO^2$: 1Aq.; $c = 6KO, 1NaO, 1CaO, 2CuO, 20MnO, 150MnO^2 + 30Aq. = 1$ base : $5MnO^2$: 1Aq.; *d* and *e* $= BaO, 2MnO, 6MnO^2 + 3Aq. = 1$ Base : MnO^2 : 1Aq. Hence *a*, then *b* and *c*, and lastly *d* and *e*, form three different varieties.

2. *Varvicite.*—Texture crystalline-laminated; specific gravity from 4·531 to 4·623; resembles Manganite in appearance, and Pyrolusite in hardness and in the colour of its powder.

	Calculation.		Phillips.
			a.
4Mn	112	63·27	63·0
7O	56	31·64	31·6
HO	9	5·09	5·4
	177	100·00	100·0

Or:			Turner.	
			b.	*c.*
$4Mn^3O^4$	464	87·38	86·89	86·87
5O	40	7·53	7·39	8·15
3HO	27	5·09	5·72	4·98
	531	100·00	100·00	100·00

$MnO, 3MnO^2 + Aq.$—*a* and *b* are from Warwickshire, *c* from Ilefeld. (R. Phillips and Turner, *Phil. Mag. Ann.* 5, 209 and 254; 6, 281; 7, 284.)

D. PEROXIDE OF MANGANESE. MnO.

Manganhyperoxyd, Peroxyde de Manganese.—Found native as *Pyrolusite, Grey Oxide of Manganese* (*Graubraunsteinerz*) *Soft Manganese* (*Weichmangan or Braunstein*).

Preparation.—Manganoso-manganic or manganic oxide is boiled with strong nitric acid.—2. Nitrate of manganous oxide is gradually heated to incipient redness, and the residue pounded and freed by boiling nitric acid from any remaining manganous oxide; the insoluble residue is then washed and very carefully heated to low redness, stirring all the while. (Berthier.)—3. Carbonate of manganous oxide is heated in an open vessel to 260°, and any portions of carbonate which may then remain undecomposed, are removed by cold and very dilute hydrochloric acid; whereupon, according to Forchhammer, pure peroxide remains behind.—4. Carbonate of manganous oxide is carefully heated with fused chlorate of potash, and the mass, when cold, well washed with water. (Göbel, *Schw.* 67, 177.)—5. A solution of a manganous salt, even when very dilute, provided it is perfectly free from iron, deposits peroxide of manganese on the positive pole of a voltaic battery; a feeble current is sufficient for the purpose. (Fischer, *Kastn. Arch.* 16, 219.)

Pyrolusite has the same crystalline form as manganite. It appears to be formed from the latter by absorption of oxygen and loss of water; for many crystals are formed externally of pyrolusite, and internally of manganite. (Haidinger, *Pogg.* 11, 374.) Pyrolusite is somewhat softer than manganite, and of specific gravity from 4·7 to 4·94; it has a steel-grey colour inclining to iron-black; its powder is grey. The artificially prepared peroxide is black, with metallic lustre, hard, and tough. (Berthier.)

	Calculation.		Forchhammer.	Berzelius & Arfvedson.
Mn	28	63·64	63·65	64·02
2O	16	36·36	36·35	35·98
MnO^2	44	100·00	100·00	100·00

Or:			Turner.	
			Elgersburg.	Ilefeld.
Mn^3O^4	116	87·88	86·06	85·62
2O	16	12·12	11·78	11·60
BaO			0·53	0·66
SiO^2			0·51	0·55
HO			1·12	1·57
CaCl				trace
$3MnO^2$	132	100·00	100·00	100·00

($MnO^2 = 345·89 + 2 \,.\, 100 = 545·89$. Berzelius.)

Pyrolusite frequently contains manganite, psilomelane, (and with it also baryta, copper, &c.) sesquioxide of iron, alumina, quartz, and carbonate of lime; also sulphate of lime and chloride of calcium; whence, according to R. Phillips (*Phil. Mag. Ann.* 1, 314), native peroxide of manganese, unless previously washed with water, frequently evolves chlorine when treated with oil of vitriol; in other cases, however, the chlorine arises from hydrochloric acid contained in the oil of vitriol.

(II., 181, 182.) [For the mode of ascertaining the per-centage of peroxide of manganese in the various minerals which contain it, *vid.* Levol, *Ann. Pharm.* 44, 355; also Fresenius and Will, *Ann. Pharm.* 49, 125.]

Decompositions.—1. When peroxide of manganese is even gently ignited, a portion of its oxygen is expelled in the gaseous form, and sesquioxide left behind; at a higher temperature, ⅔ at., or 12·12 per cent. (according to Berthier, 11·8 to 12 per cent.,) is given off, leaving manganoso-manganic oxide.—2. When ignited in a charcoal crucible, it yields 82 per cent. of protoxide. (Berthier.)—3. By heating with sulphur it is resolved, with disengagement of sulphurous acid gas, into a compound of manganous oxide with sulphide of manganese.—4. When heated with oil of vitriol, it first evolves one-fourth of its oxygen, and is converted into manganic sulphate (*vid.* Hess, *Pogg.* 52, 116); afterwards, when the heat is increased, another fourth of the oxygen is given off, and manganous sulphate formed. (*Sch.* 16.) Strong boiling sulphuric acid dissolves it, converting it into manganous oxide and liberating oxygen gas. —5. Hot hydrochloric acid dissolves it, with evolution of chlorine and formation of protochloride of manganese or hydrochlorate of manganous oxide. (*Sch.* 64 and 73.)—6. It is also dissolved by hydrated sulphurous acid, with formation of hyposulphate (II., 174) and sulphate of manganous oxide ($MnO^2 + SO^2 = MnO, SO^3$); and by hydrated nitrous acid, with formation of nitrate of manganous oxide. Nitric oxide, according to Kastner (*Kastn. Arch.* 26, 165) acts in a similar manner, provided water is present. By the addition of organic substances, such as oxalic acid, sugar, &c., the carbon of which combines with the second atom of oxygen, the solution of peroxide of manganese in nitric and sulphuric acids is greatly facilitated.—7. By igniting peroxide of manganese with hydrate of potash in a close vessel, manganate of potash and manganic oxide are produced. (Forchhammer, Mitscherlich.)

Combinations.—*a.* With Water.—HYDRATED PEROXIDE OF MANGANESE.

α. One-fourth hydrated, $4MnO^2,HO$.—Hydrated manganic oxide, or the hydrated peroxide *γ*, is boiled in moderately concentrated nitric acid, and afterwards washed and dried over a water-bath.—Brownish-black, dense, tenacious masses, having an earthy fracture. (Berthier.)

		Calculation.
$4MnO^2$	176	95·13
HO	9	4·87
$4MnO^2,HO$	185	100·00

Or:			Berthier.	Rammelsberg.
$4Mn^3O^4$	464	83·60	84·0	84·1
$8O$	64	11·53	11·5	11·3
$3HO$	27	4·87	4·5	4·6
	555	100·00	100·0	100·0

β. Trihydrated.—$3MnO^2,HO$.—Separates spontaneously after a short time from a solution of manganous bromate, in the form of a black powder, which gives off the whole of its water, even at a temperature of 200°. (Rammelsberg, *Pogg.* 55, 67.)

	Calculation.		Or:			Rammelsberg.
$3MnO^2$	132	93·62	Mn^3O^4	116	82·27	93·76
HO	9	6·38	$2O$	16	11·35	
			HO	9	6·38	6·24
$3MnO^2,HO$	141	100·00		141	100·00	100·00

γ. *Dihydrated.*—$2MnO^2,HO$.—1. Carbonate of manganous oxide is diffused in water, and chlorine gas passed through it uninterruptedly and in large excess, so that the liquid after 24 hours still contains free chlorine; any manganous carbonate remaining in the precipitate is removed by cold dilute acetic or nitric acid, and the residue washed and dried.—2. A salt of manganous oxide is precipitated by chloride of soda or chloride of lime, and the precipitate washed with water and dried. (R. Phillips, *Phil. Mag. Ann.* 5, 216; E. Dingler, *Kastn. Arch.* 18, 252; Winkelblech, *Ann. Pharm.* 13, 262.) According to Schaffner (*Ann. Pharm.* 51, 168) this method yields the tribasic hydrate.—The black hydrate, precipitated by Pelouze from salts of manganous oxide by hypochlorous acid is probably the same compound.—¶ 3. Schaffner (*Ann. Pharm.* 51, 168) likewise obtained it by adding chloride of ammonium and free ammonia to a solution of manganous sulphate, and leaving the mixture exposed to the air. After some time, a leather-brown precipitate is formed, which retains its colour on drying. ¶—Dark brown, loosely coherent powder, consisting of shining spangles; stains the skin, &c.; does not cohere into masses when heated in a water-bath. (Berthier.) Reddish brown, very friable mass. (Winkelblech.) When heated to dull redness, it gives off water and oxygen gas at the same time. By boiling with moderately strong nitric acid, which dissolves a small quantity of protoxide with evolution of oxygen gas, it is converted into the compound α. (Berthier.) Does not dissolve completely in boiling nitric acid. Oxalic acid decomposes it rapidly, with great rise of temperature. (Winkelblech.)

	Calculation.	
$2MnO^2$	88	90·72
HO	9	9·28
$2MnO^2,HO$	97	100·00

Or:			Winkelblech.	Berthier.	Dingler.
$2Mn^3O^4$	232	79·72	90·49	77	77
$4O$	32	11·00		11	11
$3HO$	27	9·28	9·40	12	12
	291	100·00	99·89	100	100

According to Berthier and Dingler, who dried the hydrate for analysis at 100°, the formula is not $2MnO^2,HO$, but $3MnO^2,2HO$.

δ. *Monohydrated.*—MnO^2, HO.—1. Formed by boiling hydrated manganic oxide in dilute nitric acid. (Forchhammer.)—2. By boiling manganate or permanganate of potash with excess of sulphuric or nitric acid, till the hydrate is precipitated. (Mitscherlich.)—As prepared by the second method, it is brownish black; with an aqueous solution of sulphurous acid, it yields nearly pure manganous hyposulphate, and only a smal quantity of sulphate. (Mitscherlich.)

	Calculation.			Or:			Mitscherlich.
MnO^2	44	83·02	Mn^3O^4	116	72·96	72·57
HO	9	16·98	2O	16	10·06	9·88
			3HO	27	16·98	17·55
MnO^2,HO	53	100·00		159	100·00	100·00

Ores of Manganese, principally containing hydrated Peroxide.

To this class belong most varieties of *Wad.* The varying admixture of some of the lower oxides of manganese (manganoso-manganic or manganic oxide), as also of baryta, ferric oxide, &c. does not allow of any stoïchiometrical calculation of these imperfectly crystallized minerals. It is sufficient, therefore, to give the results of some of the analyses.

	Turner.			Berthier.		
	a.	*b.*		*c.*	*d.*	*e.*
Mn^3O^4	79·12	87·245	MnO	62·4	68·9	46·5
O	8·82	9·675	O	12·8	11·7	7·1
HO	10·66	3·080	HO	15·8	12·4	8·8
BaO	1·40	trace	Fe^2O^3	6·0	7·0	3·6
			Clay	3·0		
			Quartz			33·6
	100·00	100·000		100·0	100·0	99·6

a is Wad from Upton Pyne, consisting of loosely agglomerated brown scales; specific gravity, 2·314. Similar to the above, in properties and composition, is the Wad of Hüttenberg, in Carinthia, from Nassau and from Elbingerode; the oxygen in *a* is not sufficient to convert all the manganoso-manganic oxide into peroxide.—*b* is *Ochrey Wad;* probably a mixture of hydrated sesquioxide and anhydrous peroxide; if so, it does not belong to this head. (Turner, *N. Edinb. J. of Sc.* 2, 213.)—*c* occurs at Grosvi, in brownish black, dull masses, which yield a reddish brown powder. When ignited, it loses 24 per cent. of water and oxygen; dissolves slowly in oil of vitriol, forming a violet-coloured solution; evolves chlorine, even with cold hydrochloric acid, and more readily than other varieties of the peroxide.—*d* is Wad from Vicdessos, occurring in light, soft, warty masses, which leave a deep stain when rubbed. Before analysis, it was freed from carbonate of lime by digestion in cold acetic acid; by ignition, it lost 19 per cent. of oxygen and water.—*e*, from Graubundten; compact, with dense granular fracture; sometimes with metallic lustre, and black; sometimes dull and brown. (Berthier, *Ann. Chim. Phys.* 51, 91.)

E. MANGANIC ACID. MnO^3.

Mangansaüre, Acide Manganique.

Formation.—1. By igniting manganese or one of its oxides with a fixed alkali in contact with air, or with chlorate of potash, or with a fixed alkaline nitrate.—Peroxide of manganese, ignited with hydrate of potash, even out of contact of air, yields manganate of potash, because a portion of the peroxide is converted into sesquioxide.

Not known in the separate state.

	Calculation, according to Mitscherlich.		Forchhammer.
Mn	28	53·85	50·8
3O	24	46·15	49·2
MnO^3	52	100·00	100·0

$$MnO^3 = 345{\cdot}89 + 3 \,.\, 100 = 645{\cdot}89.$$ (Berzelius.)

Combinations.—With Salifiable Bases, forming salts called MANGANATES. The potash, soda, baryta, and strontia-salts are nearly all that are known; they are obtained by the method given for the preparation of manganic acid. They are of a dark bluish green colour. They detonate on glowing coals. The first two are soluble in water, and form deep green solutions. The solution is permanent when it contains an excess of alkali; but if the alkali is not in excess, the liquid turns red, and with greater rapidity in proportion to the quantity of water present, and to the facility with which the carbonic acid in the air has access to the alkali. In this case, the alkaline manganate is resolved into permanganate—which remains in solution and colours it red, together with free potash or carbonate of potash—and insoluble hydrated peroxide of manganese. ¶ Schönbein regards the so-called salts of manganic acid as compounds of peroxide of manganese and peroxide of the electro-positive metal:—thus, manganate of baryta, according to his view, is $MnO^2 + BaO^2$, and is resolved by acids into a salt of baryta and a compound of peroxide of manganese and peroxide of hydrogen. ¶

$$3(KO,MnO^3) = KO,Mn^2O^7 + MnO^2 + 2KO.$$

By the addition of an acid, the decomposition and red colour are instantly produced; with hydrochloric acid, the red colour soon passes into brown, from formation of hydrochlorate of manganic oxide. Sulphurous and hydrosulphuric acid decolorize the green solution by deoxidizing the manganic acid.

F. PERMANGANIC ACID. Mn^2O^7.

Hypermanganic acid, Uebermangansäure, Oxymangansäure, Acide Oxymanganique.

Formation.—1. By the decomposition of salts of manganic acid.—2. By bringing chlorine in contact with an oxide of manganese and a fixed alkali in solution. Hence, in the preparation of chlorate of potash with chlorine gas, if chloride of manganese passes over into the aqueous solution of carbonate of potash, the solution acquires a red tint.—3. By digesting a salt of manganous oxide with sulphuric acid and peroxide of lead. (Forchhammer.)

This acid has not yet been isolated.

¶ According to Schönbein, that which has hitherto been regarded as permanganic acid is really a compound of peroxide of manganese and peroxide of hydrogen, or ozone, according to the formula $2MnO^2 + 3HO^2$,—inasmuch as, with deoxidizing agents, the so-called permanganic acid behaves exactly like peroxide of hydrogen, or ozone itself. (*Vid. Decomposition of hypermanganic acid,* infra.) (Schönbein.) ¶

	Calculation, According to Mitscherlich.		Forchhammer.	Unverdorben.	Fromherz.
2Mn	56	50	43·1	58·74	59·45
7O	56	50	56·9	41·26	40·55
Mn^2O^7	112	100	100·0	100·00	100·00

$Mn^2O^7 = 2 \,.\, 345{\cdot}89 + 7 \,.\, 100 = 1391{\cdot}78$. (Berzelius.)

Combinations.—*a.* With Water. AQUEOUS PERMANGANIC ACID.—*Preparation.*—1. From an aqueous solution of permanganate of baryta, the baryta is precipitated by an equivalent quantity of sulphuric acid, and the clear liquid decanted. (Mitscherlich.)—2. Carbonic acid gas is passed through manganate of baryta diffused in 30 parts of water, stirring frequently, till the green colour of the powder is changed into brown. (This brown powder is a mixture of carbonate of baryta, hydrated peroxide of manganese, and portions of undecomposed manganate of baryta.) The decanted dark violet solution, which, besides permanganic acid, contains acid permanganate and acid carbonate of baryta, is boiled for a quarter of an hour to expel carbonic acid and precipitate the carbonate of baryta; the small quantity of baryta still held in solution by the permanganic acid is then removed by a few drops of dilute sulphuric acid; the solution decanted, and boiled down to three-fourths of its bulk, and lastly poured off from the precipitated hydrate of peroxide of manganese. (Fromherz.) If the solution is evaporated in vacuo over oil of vitriol, brown oxide of manganese is obtained; but when evaporated at a gentle heat, it yields, on cooling, small dark carmine-red needles containing 8·411 per cent. of water, which Fromherz regards as crystallized permanganic acid. Mitscherlich and Wöhler consider these crystals as acid permanganate of baryta, since pure permanganic acid is decomposed by boiling its aqueous solution, and cannot be obtained in the crystalline state. (*Pogg.* 25, 297; 31, 677; 32, 80.) On the other hand, the existence of a crystallized acid permanganate of baryta is improbable; and the neutral salt would not be decomposed in vacuo. The subject deserves further investigation.—3. The green solution of mineral chameleon is precipitated by nitrate of lead, and the precipitate, which consists of sesquioxide of manganese and peroxide of lead—after being washed but not dried—is decomposed by long digestion with a mixture of one part of oil of vitriol and ten parts of water, added in quantity not sufficient for complete saturation. (Forchhammer.) Under these circumstances, the greater part of the manganic acid is decomposed, especially after the sulphuric acid has been completely saturated by the oxide of lead. (Fromherz.)—4. Hünefeld (*Schw.* 60, 133) decomposes manganate of baryta by phosphoric acid. In this process, however, the presence of phosphoric acid and baryta in the permanganic acid is scarcely to be avoided.

Properties.—Beautifully coloured liquid, which appears dark carmine-red by reflected, and dark violet by transmitted light; when somewhat dilute, it is reddish blue, and a still larger addition of water gives it a carmine colour. The acid imparts a distinct red colour to very large quantities of water. (Fromherz.) It is inodorous, and has at first a sweet, and afterwards a bitter, rough taste (Fromherz): its taste is pungent and disagreeable. (Forchhammer.) It stains the skin brown, but does not redden litmus (Fromherz); destroys the colour of litmus and turmeric paper, at the same time turning them brown, from deposition of hydrated peroxide of manganese. (Forchammer, Mitscherlich.)

Decompositions.—1. The aqueous solution deposits manganic oxide when heated or exposed to light; it is partially decomposed at 45°, and completely at 100°,—more rapidly also in proportion to the degree of dilution; a concentrated solution may be boiled for many hours without sensible decomposition. (Fromherz.) The solution is slowly decomposed at about 20°, and rapidly between 30° and 40°, yielding oxygen gas and insoluble hydrated peroxide of manganese; the decomposition is completed by boiling. (Mitscherlich.) Forchhammer detected an electrical odour [ozone?] when the solution was evaporated or exposed to the sun's rays.—2. Many substances remove oxygen gas from aqueous permanganic acid at ordinary temperatures, and throw down manganoso-manganic oxide [or hydrated peroxide of manganese?]. Hydrogen gas passed through the solution decomposes it rapidly, with formation of water; recently ignited charcoal, rapidly, without evolution of gas; phosphorus gradually, and phosphuretted hydrogen, immediately, with formation of phosphoric acid; sulphur, in the course of a few days, with formation of sulphuric acid; hydrosulphuric acid in excess, with separation of milk of sulphur, and formation of water and sulphuric acid, which dissolves a portion of protoxide of manganese (a small quantity of hydrosulpuric acid produces a brown colour, and in a few minutes separates brown oxide of manganese, after which the solution exhibits a pale rose colour); bisulphide of carbon, with formation of sulphuric acid and probably also of carbonic acid [many metallic sulphides are converted into sulphates by hypermanganic acid]; iodine, at a moderate heat, with formation of iodic acid*. Zinc and iron decompose the acid in the course of a few days; antimony, bismuth, lead, copper, mercury, and silver, in about four weeks, being themselves converted into oxides. Sesquioxide of chromium, teroxide of antimony, protoxide of tin, protoxide of manganese, the yellow and red oxides of lead, protoxide of iron, dioxide of copper and dioxide of mercury (generally, when used in the hydrated state) these oxides themselves rising to a higher degree of oxidation; arsenious acid, which is thereby converted into arsenic acid, the solution, however, remaining brown; ferrocyanide of potassium, with formation of ferricyanide; olefiant gas, immediately, with formation of carbonic acid, and probably also of water; alcohol and ether, apparently with evolution of carbonic oxide gas; sugar, gum, woody fibre, paper, with formation of carbonic acid; camphor, oil of turpentine (the latter very quickly), turpentine, colophony, vegetable oil, without evolution of gas, and probably, therefore, with formation of water; stearic acid, oleic acid, morphia, urea, the colouring matter of blood, gelatine, albumen, and fibrine; likewise precipitate brown oxide of manganese from permanganic acid. (Fromherz.) Sulphate of indigo, and the infusions of galls, saffron, logwood, madder, columbo, rhubarb, quassia, aloes, and Peruvian bark, are turned brown, and their colouring matter is destroyed. (Fromherz.)—3. Other substances, by a more powerful attraction for oxygen, completely convert the permanganic acid into protoxide of manganese, which then remains dissolved. Thus: sulphurous and nitrous acids—instantly, with formation of sulphate or nitrate of manganous oxide; hydriodic acid—producing a reddish brown liquid, which contains protiodide of manganese, together with free iodine (when a smaller quantity of the hydriodic acid is used, brown oxide of manganese is precipitated, and the brown solution contains free iodine); hydrochloric acid—with formation of protochloride of manganese and evolution of chlorine; chloride of sulphur—rapidly, with separation of sulphur and formation of manganous sulphate; oxalic, tartaric, and acetic acids—with formation of a manganous salt. (Fromherz.) [According to Unverdorben, acetic acid produces no effect; according to the author's own experiments, it acts very slowly.] The following substances do not decompose permanganic acid:—tin, chlorine, carbonic acid, boracic, phosphoric, sulphuric, nitric, chromic, arsenic (Fromherz), or bromic acid. (Rammelsberg.)

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* ¶ The action of iodide of potassium is peculiar: when aqueous hypermanganic acid is poured into a solution of this salt, a large quantity of reddish brown peroxide is immediately thrown down, and the liquid assumes a brown colour, from separation of iodine: if now the filtered solution be heated till the whole of the free iodine is expelled, and very dilute sulphuric or phosphoric acid afterwards added, a fresh quantity of iodine is precipitated—thus proving that iodate of potash and peroxide of potassium must be contained in the liquid. This reaction is precisely similar to that of iodide of potassium with peroxide of hydrogen or ozone. Caustic potash behaves nearly in a similar manner, peroxide of manganese being precipitated and the filtrate containing peroxide of potassium. (Schönbein.) Finely divided platinum decomposes permanganic acid rapidly. ¶

b. With Salifiable Bases, forming salts called PERMANGANATES or OXYMANGANATES. The potash and soda salts are formed by the spontaneous decomposition of the corresponding alkaline manganates dissolved in water. Most of the others are obtained by saturating aqueous permanganic acid with such bases as have no tendency to combine with another atom of oxygen; or, according to Mitscherlich, by rubbing together in a mortar finely pounded permanganate of silver and a solution of the hydrochlorate of the base, and decanting from the insoluble chloride of silver produced. All filtration is to be avoided, on account of the deoxidizing action of paper. The permanganates, in the anhydrous state, are dark red or brownish black. They detonate with combustible bodies, like the nitrates and chlorates, sometimes even by mere friction, the acid being generally reduced to the state of protoxide of manganese. Sulphuric or phosphoric acid separates the permanganic acid from the base; the acid, however, is soon resolved into oxygen gas and peroxide of manganese, which is deposited at the bottom of the vessel. (Chevillot & Edwards.) Hydrochloric acid gives off chlorine, and throws down sesquioxide or peroxide of manganese, which, on heating the mixture, is again dissolved, as protochloride, with fresh evolution of chlorine. All the permanganates are soluble in water, and many are likewise deliquescent; the least soluble is the permanganate of silver; hence, on mixing the concentrated solution of another permanganate with nitrate of silver, the permanganate of silver is precipitated almost completely, and in the crystalline form. (Mitscherlich.) The aqueous solutions of the permanganates, like that of permanganic acid itself, have an intense red colour, which is still perceptible even after considerable dilution. They are decomposed and decolorized by almost all substances which decompose aqueous permanganic acid, those, namely, which are enumerated under (2) and (3). (Fromherz.)—Ammonia decolorizes them immediately, with evolution of nitrogen gas; organic colouring matters are more slowly destroyed by them than by the free acid. (Mitscherlich.) Sulphurous and phosphorous acids decolorize the permanganates rapidly, forming salts of the protoxide. Hydrosulphuric acid precipitates a light-coloured mixture of sulphur and hydrated sulphide of manganese; hydrosulphate of ammonia in excess throws down flesh-coloured hydrated sulphide of manganese. (H. Rose.)—Permanganate of potash gives no precipitate with the salts of baryta, magnesia, alumina, or with zinc, cadmium or nickel salts, or with the salts of the higher salifiable oxides of titanium, uranium, tin, iron, cobalt, copper, mercury, silver, gold, and platinum; but with salts whose bases have a tendency to absorb oxygen, as with those of sesquioxide of chromium, (which is converted into chromic acid), and of the protoxides of manganese, tin, lead, and iron, and of dioxide of mercury, permanganate of potash forms precipitates, consisting of mixtures of sesquioxide of manganese and the higher oxide of the other metal. (Fromherz.) ¶ According to Schönbein's view, the salts of permanganic acid are really compounds of peroxide of manganese and a quadoxide of the base: *e. g.* $2MnO^2 + KO^4$. In the case of potash, the existence of such an oxide, corresponding to the sulphur compound, does not appear very improbable, inasmuch as the action of ozone on potash appears to produce KO^2, and the ordinary peroxide, KO^3, may really be nothing more than $KO^2 + KO^4$. (Schönbein.) ¶

MANGANESE AND CARBON.

A. *Carbide of Manganese?*—*a.* Manganese reduced by charcoal always contains carbon, which, when the metal is dissolved, remains behind in the form of a black powder.—*b.* Sulphocyanide of manganese, when ignited, leaves a residue of MnC; and cyanide of manganese, a residue of MnC^2, in the form of a fine, very combustible powder, or if the heat is very carefully applied, in brilliant, colourless octohedrons. [?] (Brown, *J. Pr. Chem.* 17, 492.)—*c. Manganese-graphite.*—Produced by the long continued fusion of manganese in a charcoal crucible; according to Wollaston, also a large proportion of the graphite which separates from purified cast iron, consists of carbide of manganese. It has a stronger lustre than other kinds of graphite, is laminated, and may be used for writing. (John.) [It probably consists of carbon, with manganese accidentally adhering to it in small quantities.]

B. CARBONATE OF MANGANOUS OXIDE, or MANGANOUS CARBONATE. —Found native as *Manganese-spar.*—Crystalline system, the rhombohedral. Occurs in obtuse rhombohedrons. *Fig.* 141, 143, 135; $r^1 : r^3$ or r^5 (*Fig.* 141) = 73° 9′; $r^3 : r^5$ = 106° 51′. Cleavage distinct parallel to r^1. Sp. gr. 3·55 to 3·59. Of the same hardness as felspar. Translucent; of a rose-red colour and pearly lustre. Decrepitates when ignited, becomes greenish grey, and afterwards turns black, if exposed to the air, from formation of manganoso-manganic oxide: when ignited in a close vessel, it leaves greenish grey protoxide. Ignited in a current of chlorine gas, it gives off carbonic acid gas, and, according to Wöhler, is converted into a crystalline mixture of chloride of manganese and manganoso-manganic oxide:

$$4(MnO, CO^2) + Cl = MnCl + Mn^3O^4 + 4CO^2.$$

Dissolves very slowly in cold, and rapidly in warm hydrochloric acid.

	Calculation.	
MnO	36	62·07
CO^2	22	37·93
MnO,CO^2	58	100·00

	Stromeyer.		
	Kapnik.	Nagyag.	Freiberg.
CaO,CO^2	6·05	10·58	13·08
MgO,CO^2	3·31	2·43	7·26
MnO,CO^2	89·92	86·64	73·70
FeO,CO^2			5·76
HO	0·44	0·31	0·05
	99·72	99·96	99·85

Di-hydrated.—An aqueous solution of sulphate of manganous oxide, or protochloride of manganese, is precipitated with monocarbonate or bicarbonate of potash or soda, and the precipitate washed with cold boiled water, and dried in vacuo over oil of vitriol. If the precipitate is washed with water containing air, and is likewise dried in the air, a portion of the salt is converted into hydrated manganic oxide, which gives it a red-brownish white tint.—Delicate, snow-white, tasteless powder, permanent in the air. When heated to redness in an open vessel, it first turns black and then brown, from formation of manganoso-manganic oxide. By ignition with two parts of sulphur, it yields sulphurous acid and carbonic acid gas, a small quantity of manganous sulphate, and a large quantity of sulphide of manganese, mixed with a variable quantity of manganous oxide, less, however, in proportion as the mixture has been more gradually heated. (Arfvedson.) Chlorine-water expels the carbonic acid, and converts the carbonate into hydrated sesquioxide, which, if treated with a larger quantity of chlorine, is converted into hydrated peroxide of manganese. (Berthier.) When boiled with an aqueous solution of chloride of lime, it first forms manganoso-manganic oxide, and then suddenly anhydrous peroxide of manganese, together with a small quantity of permanganate of lime, which colours the solution purple-red. (Böttger, Beiträge, 2, 12.)—By a boiling solution of potash, which removes the whole of the carbonic acid, it is converted into hydrated protoxide of manganese. (Gmelin.)—When recently precipitated, it dissolves in aqueous solutions of ammoniacal salts (Wittstein); but after being precipitated for some time, it dissolves slowly, according to Wittstein, and not at all, according to Brett.—Soluble in 7680 parts of pure water, and in 3840 parts of aqueous carbonic acid. (John.)

		Calculation.		Ure.	Turner.	John.	Forchhammer.
$2MnO$	....	72	57·6	57·3	56·853	55·84	51·755
$2CO^2$	....	44	35·2	35·4	34·720	34·16	33·050
HO	....	9	7·2	7·3	8·427	10·00	13·520
$2(MnO,CO^2) + Aq.$		125	100·0	100·0	100·000	100·00	98·325

The salt analysed by Ure was dried in the air at a temperature of 88°; that analyzed by Turner, in vacuo over oil of vitriol.

MANGANESE AND BORON.

BORATE OF MANGANOUS OXIDE, OR MANGANOUS BORATE.—Borax gives a white precipitate with manganous salts. The presence of a magnesia-salt prevents the precipitation, and the precipitate formed in the contrary case, is soluble in an aqueous solution of sulphate of magnesia. (Berzelius.) Sexborate of potash does not affect the salts of manganous oxide. (Laurent.)

MANGANESE AND PHOSPHORUS.

A. **PHOSPHIDE OF MANGANESE.**—*a.* When manganese is ignited with an equal weight of glacial phosphoric acid, (with or without $\frac{1}{16}$ of charcoal powder), or when phosphorus is thrown on ignited manganese, a white brittle mass is obtained, having the metallic lustre and a granular texture, more fusible than manganese itself, and permanent in the air. (Pelletier.)—*b.* When phosphuretted hydrogen gas is passed over heated chloride of manganese, and the undecomposed chloride afterwards dissolved out with water, a black metallic-shining residue is left, consisting of phosphide of manganese. This compound does not exhibit a phosphorus-flame before the blow-pipe; it is insoluble in hydrochloric acid. (H. Rose, *Pogg.* 24, 335.)

B. Hypophosphite of Manganous Oxide, or Manganous Hypophosphite.—Formed when an aqueous solution of hypophosphite of lime is boiled, for a long time, with excess of manganous oxalate. The filtrate yields, on evaporation, an amorphous mass, which swells up when heated, and evolves spontaneously inflammable phosphuretted hydrogen gas. (H. Rose, *Pogg.* 12, 87.)

C. Phosphite of Manganous Oxide, or Manganous Phosphite.—Terchloride of phosphorus dissolved in water and neutralized with ammonia, gives with hydrochlorate or sulphate of manganous oxide, provided the manganous salt is not in excess, a reddish white precipitate, which, after drying, resembles dried compact hydrate of alumina.

	Calculation.		H. Rose.
$2MnO$	72·0	49·52	50·19
PO^3	55·4	38·10	38·02
$2HO$	18·0	12·38	11·79
$2MnO,PO^3+Aq.$	145·4	100·00	100·00

By drying at a rather elevated temperature, one atom of water is expelled from the salt. (H. Rose.)

Manganous phosphate, when ignited in a retort, often becomes suddenly incandescent, this appearance being the more quickly produced, the more carefully the salt has been dried. Under these circumstances, it gives off hydrogen gas charged with phosphorus, the quantity of which is greater as the salt is drier; the gas, however, is not spontaneously inflammable. A trace of phosphorus sublimes at the same time, and the residue in the retort consists of manganous phosphate, with from 1 to 3 per cent. of blackish brown phosphoric oxide. In the residual manganous phosphate, more than 2 and less than 3 atoms of manganous oxide are combined with one atom of phosphoric acid. If the salt has been distilled after drying, the residue contains less phosphoric acid; if it be distilled in the moist state, it yields no sublimed phosphorus, and the residue contains less phosphoric oxide and a larger proportion of phosphoric acid.—100 parts of the salt evaporated to dryness with nitric acid, and ignited, leave 99·24 parts of ignited manganous phosphate, 2 atoms of oxygen replacing the 2 atoms of water. The salt is sparingly soluble in water: it dissolves in an aqueous solution of hydrochlorate or sulphate of manganous oxide. (H. Rose, *Pogg.* 9, 33, & 224.)

D. Phosphate of Manganous Oxide, or Manganous Phosphate.—When phosphate of soda is added to solution of manganous sulphate, this salt is precipitated in the form of a white powder (which does not appear crystalline under the microscope: *Heintz*). Boiling solution of potash removes the whole of the phosphoric acid. Water dissolves this compound sparingly; solution of carbonate of ammonia, somewhat more freely; from the latter solution it is again deposited on boiling. (Berzelius.) It is partially soluble in hydrochlorate or nitrate of ammonia

(Brett); also in sulphate and succinate of ammonia, the liquid, however, showing a turbidity which is not removed even by heat. The solution in carbonate of ammonia is clear at first, but becomes turbid after a while, the turbidity being increased by heating the liquid.

¶ According to Heintz, this salt is composed of 3 atoms of manganous oxide, 1 atom of phosphoric acid, and 7 atoms of water, 4 of which are given off at 120°, and the 3 others at a red heat. It is insoluble in alcohol, but soluble in acetic acid, and, with greater facility, in the stronger mineral acids.

b. Diphosphate.—$2MnO,HO,PO^5 + 6Aq.$—1. Prepared by precipitating a solution of manganous sulphate with a slight excess of phosphate of soda; dividing the solution, together with the precipitate, into two equal parts; adding enough nitric or hydrochloric acid to dissolve the precipitate in one portion; and then mixing the whole together. After standing for a day or two, pale red or almost colourless crystals, having a strong glassy lustre, are deposited. These crystals appear to be tabular, right rhombic prisms, having the acute prismatic edges generally replaced by planes, so that they look like hexagonal tables. The broad terminal faces have a strong lustre, like that of apopyllite. By boiling with water, the salt is resolved into a soluble acid salt and an insoluble basic salt. (Bödeker, *Ann. Pharm.* 69, 206.)—2. By adding ordinary phosphate of soda to a solution of manganous sulphate acidulated with acetic (or with hydrochloric or phosphoric acid, in which case the precipitation is slower), till the precipitate remains permanent. Care must be taken not to throw down the whole of the manganese. The precipitate, after a while, becomes crystalline and granular, the larger crystals having a tinge of red.—3. This salt likewise forms the residue which is left on boiling an excess of the terbasic salt (*vid. infra.*) with phosphoric acid, the supernatant liquid, which contains the acid salt, being poured off, and the insoluble portion washed with water. When thus prepared, it likewise becomes crystalline after a while. The crystals dissolve readily in strong mineral acids, but with difficulty in acetic acid and in water; they are insoluble in alcohol. The salt loses 5 atoms of water between 100° and 120°, another atom at 200° or above, and the last at a red heat, so that its proper formula is probably, $2MnO, HO + PO^5 + HO + 5Aq.$ (Heintz.)

	Calculation.		Bödeker.	Heintz.
$2MnO$	72·0	34·73	34·86	34·58
PO^5	71·4	34·62	33·88	34·61
$7HO$	63·0	30·65	31·26	31·17
$2MnO,HO,PO^5+6Aq.$	206·4	100·00	100·00	100·36

c. Acid Phosphate.—$MnO,2HO,PO^5 + 2HO.$—1. Prepared by strongly heating a mixture of manganic oxide and phosphoric acid.—2. By dissolving the precipitate produced in the solution of a manganous salt by ordinary phosphate of soda, in phosphoric acid, and setting aside to crystallize.—Forms small prismatic crystals, which dissolve readily in water, and are resolved by boiling alcohol into phosphoric acid, and a salt containing 2 atoms of manganous oxide to 1 atom of acid. An aqueous solution of the salt is also precipitated by alcohol with partial decomposition. On charcoal, before the blow-pipe, it fuses readily in the outer flame, giving off phosphoric acid and phosphorus in inflammable bubbles, and yielding a black bead, which, when pressed out, appears transparent and violet-coloured; in the inner flame, the bead, after a while, becomes white and opaque, but blackens again in the outer flame. It loses 2 atoms of water between 110° and 120°, the remainder at a red heat.

	Calculation.				Heintz.
MnO	28·0	....	24·88	....	24·60
PO^5	71·4	....	49·92	....	49·17
4HO	36·0	....	25·20	....	26·01
$MnO,2HO,PO^5+2Aq.$	135·4	....	100·00	....	99·78

E. Manganous Pyrophosphate.—Formed by precipitating sulphate of manganous oxide with pyrophosphate of soda.—Amorphous, white powder, soluble in strong mineral acids, and in solution of pyrophosphate of soda.—Decomposed by potash. By dissolving it in sulphurous acid-water and boiling the solution, it is obtained in fine crystals, having a mother-of-pearl lustre.

2MnO	72·0	....	50·2	....	50·15
PO^5	71·4	....	49·8	....	49·85
$2MnO,PO^5$	143·4	....	100·0	....	100·00

(Schwarzenberg, *Ann. Pharm.* 62, 2.) ¶

F. Manganous Metaphosphate.—Precipitated, unchanged, from a solution in nitric acid by hydrosulphate of ammonia, without formation of sulphide of manganese, (Otto.)

¶ Prepared by heating sulphate of manganous oxide with pure phosphoric acid to a temperature of 316°.—Insoluble in water and dilute acids; soluble in concentrated sulphuric acid.

	Calculation.				Maddrell.
MnO	36·0	....	33·321	....	33·22
PO^5	71·4	....	66·679	....	66·78
MnO,PO^5	107·4	....	100·000	....	100·00

(Maddrell, *Mem. Chem. Soc.* 3, 273). ¶

G. Phosphate of Manganic Oxide, or Manganic Phosphate.—Manganoso-manganic oxide, or peroxide of manganese, heated nearly to redness with concentrated phosphoric acid, yields a bright violet-coloured mass, which is semifluid while hot and solid when cold. With water it forms a columbine-red solution, which is not decomposed by the addition of a large quantity of water, but is immediately decolorized by hydrosulphuric or sulphurous acid. After long standing, the solution deposits light brown-red crystalline grains.—When manganoso-manganic oxide or the peroxide is heated to full redness with excess of phosphoric acid, a peach-blossom coloured mass insoluble in water remains, from which solution of potash separates brown oxide of manganese, probably manganic metaphosphate. (Gmelin.)

¶ Hermann (*Pogg.* 74, 303.) finds that when manganic oxide (obtained by igniting the nitrate of manganous oxide, resulting from the mutual decomposition of manganous sulphate and nitrate of baryta), is mixed with aqueous phosphoric acid, the mixture evaporated to dryness, and the residue heated nearly to redness, a violet-coloured mass is obtained, which dissolves partially in water, forming a columbine-red solution and leaving a peach-blossom coloured powder. The solution, after long standing, deposits light brown crystalline grains (easily washed with water) mixed with a black substance, probably consisting of hydrated peroxide of manganese. In consequence of this admixture, the crystalline grains did not yield constant results when analyzed; they appear, however, to contain from 35·12 to 37·35 per cent. of manganic oxide, and from 48·99 to 49·91 of phosphoric acid. The peach-blossom coloured powder is insoluble in all acids excepting the hydrochloric; caustic potash, aided by heat, readily separates manganic oxide from it. By strong ignition, it is reduced to a violet glass, with loss (in a covered crucible) of 6·10 per cent.

	Calculation.			Hermann. 1.		Hermann. 2.
Mn^2O^3	80·0	25·43	....	25·57	....	25·37
$3PO^5$	214·2	68·78	....	68·25	....	69·01
$2HO$	18·0	5·79	....	6·21	....	5·62
$Mn^2O^3,3PO^5,2HO$	312·2	100·00	....	100·03	....	100·00 ¶

MANGANESE AND SULPHUR.

A. SULPHIDE OF MANGANESE.—Found native in the form of *Manganese-blende*, or *Schwarzerz.*—1. Formed by passing hydrosulphuric acid gas over heated manganous oxide or sulphate, (or carbonate, *Fellenberg,*) as long as water continues to be formed. (Arfvedson.)—2. By precipitating a manganous salt with hydrosulphate of ammonia, and heating the washed and dried precipitate in a current of dry hydrosulphuric acid gas, as long as water and sulphur are given off. (Berzelius.)—3. By igniting peroxide of manganese or manganous carbonate with sulphur. The sulphide of manganese thus prepared contains a small quantity of manganous sulphate, and, moreover, an oxysulphide of manganese, the quantity of which becomes greater the more rapidly the original mixture is heated; by repeated ignition, however, with fresh quantities of sulphur, the oxide is almost entirely converted into sulphide of manganese. (Arfvedson.)—4. By heating manganous sulphate to whiteness, either with $\frac{1}{6}$ of its weight of charcoal, or in a charcoal crucible. (Döbereiner, *Schw.* 14, 208, Berthier.) In this process, also, oxysulphide of manganese may be mixed with the pure sulphide. ¶ 5. Obtained in crystals by passing the vapour of bisulphide of carbon over the native crystallized hydrate of manganic oxide, ignited in a porcelain tube. The crystals of sulphide of manganese thus obtained have the same form and nearly the same lustre as those of the hydrated oxide. They are iron-black with a tinge of green, and yield a dingy green powder. (Völker.) ¶

Native sulphide of manganese crystallizes in iron-black cubes, with cleavage parallel to the faces of a cube; it is harder than felspar, of specific gravity of 4·0, and yields a dark green powder. The artificial sulphide prepared by the second and third methods, forms a dark green powder; that prepared by the fourth, is a more bulky, fused, dark steel-grey mass, having a semi-metallic lustre, crystalline-granular fracture, and greyish green streak. (Döbereiner, Berthier.)

	Calculation.			Döbereiner. *Artificial.*		Arfvedson. *Artificial.*		Nagyag.		Del Rio. Mexico.
Mn	28	63·64	....	65·86	....	63·13	....	62·29	....	54·5
S	16	36·36	....	34·14	....	36·87	....		....	39·0
Quartz			....		....		....		....	6·5
MnS	44	100·00	....	100·00	....	100·00	....		....	100·0

The artificial sulphide turns brown in the air, even at ordinary temperatures; the native variety does not. Sulphide of manganese, when ignited in the air, is converted into sulphurous acid and manganoso-manganic oxide,—the native sulphide, however, less easily than the artificial variety. The ore from Nagyag yields 86·03 per cent. of manganoso-manganic oxide. (Arfvedson.)—When fused with excess of oxide of lead, it gives off sulphurous acid, and yields a slag consisting of oxide of lead and protoxide of manganese, a portion of lead also being reduced. (Berthier, *Ann. Chim. Phys.* 39, 252.) Detonates when heated with nitre. It is but slightly decomposed by chlorine at high temperatures, a small quantity of chloride of sulphur being formed. (H. Rose, *Pogg.* 42, 540); the sulphide prepared by the first method is resolved into chloride of sulphur and rose-coloured, crystalline chloride of manganese. (Fellenberg, *Pogg.* 50, 76.) When heated to redness in a current of aqueous vapour, it gives off hydrogen and hydrosulphuric acid gas, and is converted into manganoso-manganic oxide. (Regnault, *Ann. Chim. Phys.* 62, 381.)

$$3MnS + 4HO = Mn^3O^4 + 3HS + H.$$

With aqueous acids, even with dilute nitric or nitro-hydrochloric acid, it gives off abundance of hydrosulphuric acid.

Hydrated Sulphide of Manganese, or *Hydrosulphate of Manganous Oxide.*—Precipitated in flesh-coloured flakes on mixing a manganous salt in solution with an alkaline hydrosulphate*. When the solution is largely diluted, the precipitate appears white for the first few moments. Hydrosulphite of ammonia likewise produces a flesh-coloured precipitate. (Wackenroder.)—The precipitate, when washed and dried in the air, turns brown from oxidation. When heated to redness in a retort, it is resolved into water and anhydrous green sulphide of manganese. (Berzelius.) It precipitates sulphate of cadmium, acetate of lead, hydrochlorate of ferric oxide, nitrate of cobalt, nitrate of nickel, nitrate of silver, and sulphate of copper. (Anthon, *J. Pr. Chem.* 10, 353.) The metals contained in these salts are probably precipitated in the form of sulphides, with formation of manganous salts. Hydrosulphate of manganous oxide turns white when boiled with potash (Wackenroder) [the alkali withdrawing the hydrosulphuric acid; *Gmelin*]. It dissolves in sulphuric, hydrochloric, and dilute nitric acid, with evolution of hydrosulphuric acid gas; also in aqueous sulphurous acid (Berthier), with separation of sulphur and formation of manganous hyposulphite†. (Rammelsberg.) [In this case no sulphuretted hydrogen is evolved, and the solution contains manganous sulphate.] Hydrosulphate of manganous oxide is slightly soluble in hydrosulphate of ammonia, but not when it contains excess of sulphur. Hence, when a manganous salt is precipitated by a large excess of hydrosulphate of ammonia, the filtrate, on being exposed to the air, or mixed with hydrosulphite of ammonia, deposits a further quantity of hydrated sulphide of manganese. (Wackenroder.)

B. OXYSULPHIDE OF MANGANESE MnS,MnO. Formed by passing hydrogen gas over red-hot manganous sulphate. 100 parts of the anhydrous sulphate yield water, sulphurous acid, and 52·78 parts of oxysulphide of manganese. This compound is also formed, together with pure sulphide of manganese, when an oxide of manganese is ignited with sulphur. Pale green powder, of a lighter colour than sulphide of manganese. (Arfvedson.)

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* ¶ By passing a current of hydrosulphuric acid gas through a solution of manganous acetate, a reddish precipitate is obtained, which contains from 2 to 2·5 per cent. of water. ¶

† It is likewise soluble in acetic acid—a property which is made use of in separating manganese from nickel and cobalt. (*Ann. Pharm.* 42, 347.)

	Calculation.		Arfvedson.	Or:			Arfvedson.
2Mn	56	70	70·26	MnO	36	45	45
S	16	20	19·86	MnS	44	55	55
O	8	10	9·88				
MnS,MnO	80	100	100·00		80	100	100

At ordinary temperatures, it is permanent in the air; when heated, it takes fire and burns, leaving 96·27 per cent. of manganoso-manganic oxide; a strong heat, however, is required to expel the whole of the sulphur. Hydrosulphuric acid gas passed over it at a red heat, rapidly decomposes it into water and 109·34 per cent. of sulphide of manganese. Acids dissolve it with evolution of hydrosulphuric acid. (Arfvedson.)

C. Hyposulphite of Manganous Oxide, or Manganous Hyposulphite.—When hyposulphite of baryta is precipitated by sulphate of manganous oxide, and the filtrate left to evaporate in the air, or under a bell-jar over oil of vitriol, the salt is almost wholly resolved into free sulphur and manganous sulphate. Alcohol added to the filtrate precipitates a concentrated solution of the salt.—2. Recently precipitated sulphide of manganese diffused in water, is rapidly converted by a current of sulphurous acid gas into the same salt, with separation of sulphur. (Rammelsberg, *Pogg.* 56, 305.)

D. Sulphite of Manganous Oxide, or Manganous Sulphite.—Sulphurous acid gas is passed through water in which manganous carbonate is diffused till the liquid emits a powerful odour of the acid (John); or the carbonate is dissolved in an excess of aqueous sulphurous acid, and the liquid boiled till the non-acid salt is precipitated. (Berthier, *N. Ann. Chim. Phys.* 7, 78.) White, crystalline-granular powder (amorphous when prepared by the second process: *Muspratt*), tasteless, permanent in the air, decomposible at a red heat, and insoluble in water, alcohol (John), and ether. (Muspratt.) Very sparingly soluble in water (Heeren, Berthier); readily soluble in aqueous sulphurous acid. (Berthier.)

	Calculation.		John.	Muspratt.
MnO	36	41·86	40·2	42·03
SO^2	32	37·21	59·8	36·47
2HO	18	20·93		21·50
$MnO, SO^2+2Aq.$	86	100·00	100·0	100·00

E. Hyposulphate of Manganous Oxide, or Manganous Hyposulphate.—Formed by passing sulphurous acid gas through water in which finely divided peroxide of manganese is diffused. Berzelius first purifies the powdered manganese, by boiling it in nitric acid and washing from all traces of hydrated sesquioxide, which would yield manganous sulphate. (Vid. II., 174; *Formation of Hyposulphuric Acid.*) The manganous sulphate produced at the same time, is removed either by evaporation and crystallization; or by carefully adding baryta-water till the solution no longer gives a precipitate with chloride of barium: pure manganous hyposulphate then remains in the liquid in the form of a deliquescent salt. (Welter & Gay-Lussac.)

F. SULPHATE OF MANGANOUS OXIDE, or MANGANOUS SULPHATE.—Oil of vitriol dissolves the metal very slowly; dilute sulphuric acid, on the contrary, with great facility. By heating peroxide of manganese with oil of vitriol, oxygen gas is disengaged and the same compound produced.

Preparation.—1. Peroxide of manganese—previously freed from carbonate of lime and magnesia by boiling with dilute sulphuric acid—is heated with an equal weight of oil of vitriol, and the resulting mass gently ignited for an hour (by which means the sulphates of iron and copper formed at first are decomposed); the manganous sulphate which remains unaltered is dissolved in water, and the solution evaporated to the crystallizing point. If the solution is still found to contain any oxide of iron or copper, the former is removed by digesting the liquid with manganous carbonate, and the latter subsequently by hydrosulphuric acid.—2. Fischer ignites 1 part of peroxide of manganese with 4 parts of green vitriol (Klauer, 5 parts of the peroxide with 2 parts of dehydrated green vitriol), and then proceeds as above.

By igniting the crystals, the anhydrous salt is obtained as a white friable mass having a bitter metallic taste, and reddening litmus very feebly when dissolved. The salt sustains a continuous red heat without decomposition; when strongly ignited, it gives off oxygen gas, sulphurous acid, and anhydrous sulphuric acid, leaving manganoso-manganic oxide. When ignited with charcoal, it evolves sulphurous acid, together with three or four times the quantity of carbonic acid and carbonic oxide gases, and leaves a compound of protoxide and sulphide of manganese. (Gay-Lussac.)

	Anhydrous.		Turner.	Brandes.	Forchhammer.
MnO	36	47·37	47·33	47·7	45·62
SO^3	40	52·63	52·67	52·3	54·38
MnO,SO^3	76	100·00	100·00	100·0	100·00

Combinations with water.—The ignited salt absorbs water with great avidity, and unites with it, forming a hard mass; when exposed to the air, it takes up 3 atoms of water. (Brandes.)

α. Monohydrated.—1. Obtained by drying the pentahydrated salt in the air at a temperature between 194° and 210°. (Graham, *Phil. Mag. J.*, 6, 420.)—2. Precipitated in the form of a pale reddish-yellow powder, by rapidly boiling an acid solution. (Kühn & Ohlmann, *Schw.* 61, 239.) From a neutral solution, this compound is also precipitated on boiling. (Graham.)

	Calculation.		Graham.	Kühn & Ohlmann.
MnO	36	42·35	89·49	41·23
SO^3	40	47·06		47·26
HO	9	10·59	10·51	11·51
$MnO,SO^3 + Aq.$	85	100·00	100·00	100·00

β. Bihydrated.—Separates on melting the heptahydrated salt alone, or on boiling it with alcohol. (Brandes.) When the pentahydrated salt is dried at 115° in the air, a compound is left containing 76 parts (1 atom) of anhydrous salt to 9·92 parts (rather more than 1 atom) of water; if it be dried at ordinary temperatures in vacuo over oil of vitriol, 15·87 parts (almost 2 atoms) of water remain with 76 parts of the anhydrous salt. (Graham.)

	Calculation.		Brandes.	Graham.
MnO	36	38·30	80·9	79·12
SO^3	40	42·55		
2HO	18	19·15	19·1	20·88
$MnO, SO^3 + 2Aq.$	94	100·00	100·0	100·00

γ. *Terhydrated.*—1. Deposited in the form of a crystalline crust from a solution of manganous sulphate not quite heated to the boiling point (Graham); it frequently crystallizes also with the tetrahydrated salt in opaque white masses. (Brandes.)—2. Produced from the tetrahydrated salt by evaporation in vacuo over oil of vitriol. (Brandes.)—3. Formed when the anhydrous salt is exposed to the air till it no longer absorbs water. (Brandes.)

	Calculation.		Brandes.	
			1.	2.
MnO	36	34·95	34·75	75·62
SO^3	40	38·84	38·71	
3HO	27	26·21	26·10	24·38
$MnO, SO^3 + 3Aq.$	103	100·00	99·56	100·00

δ. *Tetrahydrated.*—Crystallizes on evaporating an aqueous solution of the salt in the air at a gentle heat, and indeed, according to Regnault, at temperatures between 20° and 30°. Large, transparent, right-rhombic, and six-sided prisms, of specific gravity 2·092, according to Kopp; the crystals, though of invariable composition, are sometimes pale rose-coloured, and sometimes colourless. The rose-coloured crystals yield a rose-coloured solution in water; the colourless crystals, a colourless solution. (Fromherz, Brandes.) Wöhler observed well-defined, rose-coloured and colourless crystals separate from the same solution.

Fromherz and Brandes attribute these differences of colour to the presence of a higher oxide of manganese in the red salt. If rose-coloured sulphate of manganous oxide be precipitated from a not very dilute solution by carbonate of potash; the washed carbonate of manganous oxide redissolved in sulphuric acid, and precipitated by carbonate of potash; again dissolved as before; and the same process repeated several times; a colourless solution is at length obtained, which yields colourless crystals. For, on each solution in sulphuric acid, a portion of the higher oxide present is resolved into oxygen gas and manganous oxide, till at last it disappears altogether. (Fromherz.) [On the other hand, the manganous carbonate is slightly oxidized by washing in the air; and if the above explanation were correct, the red salt would be decolorized by boiling with sulphuric acid, or by a current of hydrosulphuric or sulphurous acid, which is not the case.] According to Brandes, the red salt may be converted into the colourless salt by igniting, and then dissolving it in water—or by boiling it in the state of powder with alcohol or ether, and then dissolving in water—or by boiling its solution with a small quantity of sugar; the colourless solution, obtained by either of these methods, yields colourless crystals. [The salt obtained by igniting peroxide of manganese, either with fuming sulphuric acid or with English oil of vitriol, was always found by the author to yield red crystals after purification. These crystals when ignited and redissolved, again gave a red solution. The solution was not decolorized by sulphurous acid or by boiling for two hours with sugar, not even on the addition of sulphuric acid.] Brandes obtained red crystals most frequently by dissolving peroxide of manganese in sulphuric acid, after having ignited it with charcoal and oil; and colourless crystals, by simply igniting the peroxide with oil of vitriol. According to Brandenburg (*Schw.* 14, 336), the red salt is obtained by igniting peroxide of manganese with fuming sulphuric acid, and white crystals by igniting it with common oil of vitriol. Berzelius (*Jahresber.* 11, 186) attributes the difference of colour to isomerism.

	Calculation.		Mitscherlich.	Brandes. *Red.*	Brandes. *Colourless.*	John.
MnO	36	32·14	68	31·61	31·14	31·00
SO^3	40	35·72		34·61	34·14	33·66
4HO	36	32·14	32	33·78	32·53	35·34
$MnO,SO^3+4Aq.$	112	100·00	100	100·00	97·81	100·00

In vacuo over oil of vitriol, this salt gives up 1 atom of water. When heated, it decrepitates slightly and crumbles to a white powder without fusing. When boiled in the state of powder with absolute alcohol, it gives up 1 atom of water; but to cold alcohol or boiling ether it yields nothing. (Brandes, *Pogg.* 20, 556.)

ε. *Pentahydrated.*—1. Crystallizes from a solution of the salt evaporated in the air at temperatures between 7° and 20°. (Regnault, *Ann. Chim. Phys.* 76, 200.)—2. Produced by mixing the heptahydrated salt with cold absolute alcohol. (Brandes.) The crystals have the form of blue vitriol. (Mitscherlich, Regnault.)

	Calculation.		Mitscherlich.	Brandes.	Graham.
MnO,SO^3	76	62·8	61·54	62	62·48
5HO	45	37·2	38·46	38	37·52
$MnO,SO^3+5Aq.$	121	100·0	100·00	100	100·00

ζ. *Heptahydrated.*—Separates from a cold saturated solution exposed to the air at temperatures between − 4° and + 6°. (Brandes, Regnault.) Transparent, very pale red crystals (Brandes) having the form of green vitriol. (Regnault.) It is moist to the touch, and deliquesces between the fingers; melts at a temperature but little above 19°, with separation of the bihydrated salt. By exposure to the air, between 9° and 11°, it loses 4·9 per cent. of water; and between 12·5° and 15°, 18·6 per cent. (3 atoms), efflorescing at the same time to an opaque mass. To cold absolute alcohol it yields 2 atoms of water; to alcohol of 25° B., 3 atoms, first becoming soft, then hard, and lastly crumbling to a crystalline powder. To boiling absolute alcohol it gives up 4 atoms of water. Boiling alcohol of 55 per cent. leaves the bihydrated salt, which, if allowed to cool in the liquid, recombines for the most part with the water separated. Cold ether does not remove water from the salt. (Brandes.)

	Calculation.		Brandes.	John.
MnO	36	25·90	26·75	55
SO^3	40	28·77	28·34	
7HO	63	45·33	45·00	45
$MnO,SO^3+7Aq.$	139	100·00	100·09	100

η. *Aqueous solution.*—1 part of anhydrous sulphate of manganous oxide dissolves in 1·78 parts of water at 6·25°, forming a syrupy liquid. 1 part of the tetrahydrated salt dissolves at 6·25°, in 0·883 parts; at 10° in 0·79 parts; at 18·75° in 0·82 parts; at 37·5° in 0·67 parts; at 75° in 0·69 parts; and at 101° in 1·079 parts of water; whence it appears that the solubility of the salt increases up to 75°, and decreases above that temperature. A cold saturated solution boils at 102·1° and at the same time becomes turbid, from separation of a crystalline crust, which again disappears as the liquid cools. (Brandes.)

Manganous sulphate dissolves in 500 parts of alcohol of 55 per cent., but is insoluble in absolute alcohol. (Brandes, *Pogg.* 20, 556.)

G. MANGANOSO-MANGANIC SULPHATE.—Manganoso-manganic oxide (not the native hydrated sesquioxide) dissolves almost entirely in cold pure oil of vitriol or in sulphuric acid diluted with 1 or 2 parts of water, forming a fine red solution, which when diluted with water becomes carmine-red; or 1 part of peroxide or sesquioxide of manganese may be gently heated with 13 parts of oil of vitriol, till one-half the quantity of oxygen capable of being driven off is expelled, and the resulting mass dissolved in a small quantity of cold water; 1 part of the salt imparts a bright red colour to 1280 parts of water. (R. Phillips, *Phil. Mag. Ann.* 5, 214.) The liquid when heated deposits hydrated peroxide of manganese, and is converted, without disengagement of oxygen, into a colourless solution of manganous sulphate with excess of acid. With pure alkalies and alkaline carbonates, it gives a reddish brown, and with ferrocyanide of potassium a yellowish-brown precipitate. On diluting with water, brownish-black peroxide of manganese is thrown down after a while, leaving the protoxide in solution. Many deoxidizing agents convert this salt into acid sulphate of manganous oxide. The following substances decolorize the solution: sulphurous acid; nitric acid containing nitrous acid; protochloride of tin; sulphate of ferrous oxide; nitrate of mercurous oxide, with separation of white sulphate of mercuric oxide; acetic acid; alcohol; rock-oil; naphtha; oil of turpentine; oil of lavender; and starch;—oxalic acid turns the solution brown before decolorizing it; arsenious acid acts in the same manner, but likewise precipitates a brown oxide; hydrochloric and hydrosulphuric acids turn the solution brown; tartaric acid and gum render it brown and turbid. (Fromherz.) The solution may be regarded either as containing a mixture of the sulphates of manganous and manganic oxides—or, with Fromherz, as a mixture of sulphate of manganous oxide and sulphate of manganic acid. According to the latter, a similar red solution may be obtained by adding manganic acid to acid sulphate of manganous oxide. If, however, the excess of sulphuric acid is insufficient, or if too large a quantity of manganic acid is added, a brown precipitate is formed.

H. *Sulphate of Permanganic Acid?*—If to a solution of permanganate of potash, water [sulphuric acid?] is added in such quantity as to produce considerable rise of temperature, a violet vapour is disengaged, which condenses on the sides of the vessel and rapidly undergoes decomposition. (Chevillot & Edwards.) A mixture of powdered mineral chameleon (manganate of potash) or of permanganate of potash with a small quantity of oil of vitriol (when an excess of the latter is used, the result is attended with a kind of explosion) gently heated in a retort, evolves beautiful red vapours, which are very prejudicial to the lungs, and in the absence of water, are very easily resolved into oxygen gas and hydrated peroxide of manganese; but when water is present in the receiver, they are absorbed, forming a red solution. (Unverdorben, *N. Tr.* 9, 1, 36; also *Pogg.* 7, 322.) Mineral chameleon when mixed with oil of vitriol becomes heated to 130°, and evolves violet vapours, which have a peculiar powerful smell, and condense in a receiver surrounded by a freezing mixture, forming a red liquid which contains manganic and sulphuric acids. Manganic acid heated with nearly anhydrous sulphuric acid—gently at first, till a fused violet mixture is obtained, and then at a higher temperature, whereby the mixture becomes green—yields carmine-red vapours, which condense into dark carmine-red, needle-shaped crystals; these crystals are decomposed by water into sulphuric acid and sesquioxide of manganese [peroxide]. Red vapours are also obtained on heating manganate of baryta with nearly anhydrous sulphuric acid; but when the fumes evolved from fuming oil of vitriol by heat are made to pass over manganic acid, manganate of potash, or manganate of baryta, no red vapours are evolved. (Hünefeld, *Schw.* 60, 133.) Mineral chameleon prepared from materials perfectly free from chlorine likewise yields the red vapours. (Gmelin.)

I. Sulphide of Carbon and Manganese.—Protochloride of manganese yields, at first, with hydrosulphocarbonate of lime a transparent dark brown liquid, which afterwards turns yellow and deposits a reddish-yellow powder. The powder becomes darker when dried, and is resolved by distillation into carbonic acid, sulphur, and a residue of green sulphide of manganese; it dissolves sparingly in water, forming a yellow solution. (Berzelius.)

K. Hypo-sulphophosphate of Manganese. — *Mangan-sulphosubphosphit.*—MnS,PS.—Sulphide of manganese, prepared by the second method (p. 218) is introduced into the middle bulb of three, blown on a barometer tube; then covered with a stratum of protosulphide of phosphorus, PS; and the whole exposed to a gentle and continued heat, while a current of dry hydrogen gas is passed through the apparatus. As the sulphide of manganese becomes heated, it combines with the sulphide of phosphorus, and disengages so much heat, that a portion of the latter distils right and left into the outer bulbs. The sulphide of phosphorus which passes over on the side of the hydrogen apparatus is gradually conveyed back, with the hydrogen gas, to the sulphide of manganese, and saturates it completely. After the whole of the sulphide of phosphorus has been driven over, the apparatus is left to cool, the stream of hydrogen being still kept up. (*Vid.* II., 213, 214.)

The compound is yellowish-green, and yields a powder of similar colour; it forms a loosely coherent mass. When heated out of contact of air, it gives off the whole of the sulphide of phosphorus in the liquid form, at a temperature below redness, while pure sulphide of manganese remains behind. When heated in the open air, it burns with a strong phosphorus flame, leaving pure sulphide of manganese. Dissolves in hydrochloric acid, with rapid evolution of sulphuretted hydrogen gas, and separation of an orange-coloured mass of red protosulphide of phosphorus. (Berzelius, *Ann. Pharm.* 46, 147.)

MANGANESE AND SELENIUM.

A. HYDRATED SELENIDE OF MANGANESE, or HYDROSELENIATE OF MANGANOUS OXIDE.—Manganous salts give with alkaline selenides a pale red precipitate, which assumes a darker red tint when exposed to the air, from decomposition of the hydroselenic acid and separation of free selenium.

B. SELENITE OF MANGANOUS OXIDE, or MANGANOUS SELENITE.—*a. Monoselenite.*—Soft, white, easily fusible powder, which, in the fused state, is decomposed only on the admission of air, whereby the protoxide of manganese is oxidized and the acid expelled. When fused, it attacks glass more rapidly than the corresponding salts of lime and magnesia, rendering the glass full of bubbles, even below the fusing point of the latter. It is insoluble in water. (Berzelius.) ¶ Muspratt prepared this salt by dissolving carbonate of manganous oxide in selenious acid, and obtained it in the form of a white gritty powder, which yielded a colourless solution with cold, and a pink solution with hot hydrochloric acid.

	Calculation.		Muspratt.
MnO	36	32·73	
SeO^2	56	50·90	50·00
2HO	18	16·37	
$MnO,SeO^2+2Aq.$	110	100·00	

b. Biselenite.—A crystallizable compound, which dissolves readily in water, and, when heated in close vessels, gives up the second atom of acid. (Berzelius.)

MANGANESE AND IODINE.

A. IODIDE OF MANGANESE and HYDRIODATE OF MANGANOUS OXIDE.—A solution of manganous carbonate in aqueous hydriodic acid leaves a white crystalline mass, having a somewhat styptic taste. When kept from contact of air, it may be fused without decomposition; but on the admission of air, it is resolved into vapour of iodine and manganous oxide. Deliquesces in the air, and dissolves readily in water, forming a colourless solution, which on evaporation deposits white needles. The solution when exposed to the air is slightly decomposed, depositing brown flakes. Bromine and chlorine, as well as concentrated nitric or sulphuric acid, set the iodine free. (Lassaigne.)

	Calculation.		Lassaigne.
Mn	28	18·18	17·62
I	126	81·82	82·38
MnI	154	100·00	100·00

B. HYDRIODATE OF MANGANIC OXIDE.—Very finely pounded peroxide of manganese agitated with cold aqueous hydriodic acid, yields a dark yellowish-red solution, which when heated evolves iodine, and is rapidly converted into hydriodate of manganous oxide.

C. IODATE OF MANGANOUS OXIDE, or MANGANOUS IODATE.—Precipitated, on mixing highly concentrated hot solutions of acetate of manganous oxide and iodate of soda, in the form of a light red crystalline powder, which is then washed with water and dried. When ignited, it leaves manganoso-manganic oxide free from iodine. Dissolves in about 200 parts of water. (Rammelsberg, *Pogg.* 44, 558.)

	Crystallized.			Rammelsberg.
MnO	36	....	17·82	17·626
IO^5	166	....	82·18	
MnO,IO^5	202	....	100·00	

MANGANESE AND BROMINE.

A. BROMIDE OF MANGANESE.—1. Heated manganese powder absorbs bromine vapour, forming a pale rose-coloured, fused mass.—2. A solution of manganous carbonate in aqueous hydrobromic acid, evaporated and ignited in a glass tube drawn out to a point at the top, leaves a similar pale rose-coloured mass. (Löwig.) Bromide of manganese, when ignited in an open vessel, is completely decomposed, yielding bromine vapour and manganoso-manganic oxide; with sulphuric acid it evolves hydrobromic acid gas and vapour of bromine. (Löwig.)

Hydrated Bromide of Manganese, or *Hydrobromate of Manganous Oxide.*—Bromide of manganese is highly deliquescent. (Berthemot.) The hydrated compound may be prepared by dissolving carbonate of manganous oxide in hydrobromic acid (Löwig), or by digesting metallic manganese with bromine and water. (Berthemot.) The solution, evaporated at a gentle heat, leaves a light red powder (Löwig); it yields small needles, which have a pungent taste, and, when heated, first fuse in their water of crystallization and then dry up to bromide of manganese. (Berthemot, *Ann. Chim. Phys.* 44, 392.) An aqueous solution of bromine converts protoxide of manganese into black hydrate and bromide of manganese which dissolves. (Balard, *J. pr. Chem.* 4, 178.)

B. BROMATE OF MANGANOUS OXIDE, or MANGANOUS BROMATE.—A solution of manganous carbonate in aqueous bromic acid is decomposed a few moments after its formation, bromine being evolved, and the whole of the manganese precipitated in the form of hydrated peroxide. (Rammelsberg, *Pogg.* 55, 66.)

MANGANESE AND CHLORINE.

A. PROTOCHLORIDE OF MANGANESE.—1. Manganese takes fire in chlorine gas, and is converted into chloride of manganese. (H. Davy.)—2. Hydrochlorate of manganous oxide is evaporated to dryness, and the dry residue heated (Proust, *N. Gehl,* 3, 429); in order to exclude the air, the residue is heated in a glass tube, sealed at one end and drawn out to a fine point at the other (J. Davy, *Schw.* 10, 329); or in a current of hydrochloric acid gas. (Turner.)—3. Hydrochloric acid gas is passed over carbonate of manganous oxide at the ordinary temperatures of the air at first, but afterwards at a low red heat. (Arfvedson.)—Again, when chlorine gas is passed over a strongly ignited mixture of protoxide of manganese and charcoal, needles of protochloride of manganese are formed, which remain mixed with the charcoal. (H. Rose, *Pogg.* 27, 574.)

Protochloride of manganese is rose-coloured (Arfvedson, *Schw.* 42, 213); but if any sesquioxide of manganese is formed, from the admission of atmospheric air, it acquires a dirty red or brown tint. It has a crystalline-laminated texture; fuses at a red heat, forming an oily liquid, which on cooling, again solidifies in a crystalline mass; it does not volatilize below the melting point of glass. Taste saline, but not unpleasant. (Proust, H. Davy, Turner.)

	Calculation.		Turner.	Arfvedson.	Brandes.	J. Davy.
Mn	28·0	44·16	43·8	44·25	44·74	46
Cl	35·4	55·84	56·2	55·75	55·26	54
MnCl	63·4	100·00	100·0	100·00	100·00	100

When heated to redness in the air, it is decomposed (if it contains water) into hydrochloric acid gas and manganoso-manganic oxide. (J. Davy.) No free chlorine is evolved. (Gmelin.) It is not decomposed by hydrogen gas at a red heat (Arfvedson); but by phosphuretted hydrogen it is converted into hydrochloric acid and phosphide of manganese. (H. Rose.) Probably thus:

$$3MnCl + PH^3 = 3MnP + 3HCl.$$

By ignition with sulphur, it is partially converted into sulphide of manganese. (A. Vogel.) With cold oil of vitriol, it rapidly gives off the whole of its hydrochloric acid, and is converted into sulphate of manganous oxide. (A. Vogel.) From an aqueous solution of the salt, chlorine, with the aid of heat, precipitates black hydrated peroxide of manganese (John); hypochlorous acid produces a similar result, with evolution of free chlorine. (Balard.) Chloride of lime colours the solution, first red and then violet; after which, carbonate of potash changes it to green and precipitates carbonate of lime. (Pearsall.)

Hydrated Protochloride of Manganese, or *Hydrochlorate of Manganous Oxide.*—1. The metal dissolves readily in aqueous hydrochloric acid, with evolution of hydrogen gas.—2. Carbonate of manganous oxide is dissolved in aqueous hydrochloric acid.—3. Faraday heats a mixture of strongly ignited and finely powdered peroxide of manganese with sal-ammoniac, very slowly, raising the temperature at last to low redness, and dissolves out the resulting chloride of manganese with pure water. If the peroxide of manganese is in excess, the other metals mixed with it do not enter into combination with the chlorine. Before ignition, the peroxide of manganese must be purified from carbonate of lime by boiling in dilute hydrochloric acid. To render available for this purpose the solution of protochloride of manganese obtained in the preparation of chlorine from peroxide of manganese and hydrochloric acid, Everitt (*Phil. Mag. J.* 6, 193) evaporates it to dryness in a porcelain basin; heats the dry mass, stirring constantly, till it assumes an ash-grey colour and no longer evolves hydrochloric acid—by which means the chloride of iron is partly volatilized and partly resolved into hydrochloric acid gas and sesquioxide of iron; and finally exhausts the residue with water, and filters the solution;—or he boils the solution, first rendered neutral by evaporation, with carbonate of manganous oxide, which precipitates the whole of the iron. [Oxide of copper may still remain in the solution.]

The salt crystallizes with difficulty—best, however, when slowly evaporated—in rose-coloured (often colourless: *Fromherz, Brandes*), elongated, four-sided tables, bevelled at all the edges, and often with the summits truncated; specific gravity 1·56; taste burning, afterwards saline. (John.)—The crystalline form is probably the same as that of the corresponding protochloride of iron (*q. v.*).—Colourless crystals are obtained, according to Fromherz, by repeatedly precipitating the solution with carbonate of potash and redissolving the precipitated carbonate in hydrochloric acid, as mentioned under the head of *Manganous Sulphate.* (p. 222.)

	Calculation.		Brandes.	Graham.	Bucholz.
Mn	28·0	28·17	28·08	63·88	29
Cl	35·4	35·61	34·68		
4HO	36·0	36·22	37·24	36·12	42
MnCl + 4Aq.	99·4	100·00	100·00	100·00	

Or:

MnO	36·0	36·22
HCl	36·4	36·72
3HO	27·0	27·06
MnO,HCl + 3Aq.	99·4	100·00

The crystals obtained at 0° do not contain more water. (Brandes.)

When placed over oil of vitriol, either in vacuo or in a receiver containing air, the crystals lose 2 atoms of water at ordinary temperatures. (Graham.) At 25° they become white and opaque (John); between 25° and 37° they give off hygroscopic water with decrepitation, and become hard; at 37·5° they become tough; at 50° semifluid; and at 87·5° they form a mobile liquid which boils at 106°. If the mass be kept for some time at a temperature near 100°, it gives off 28 per cent. (3 atoms) of water, and leaves a white powder, which retains one atom of water. (Brandes.)

Solution of Protochloride of Manganese.—Both the anhydrous and the hydrated chloride deliquesce rapidly in the air (John), one part of the crystals absorbing 1·2 parts of water. (Brandes.) One part of the crystallized salt dissolves at 10°, in 0·66 parts; at 31·25°, in 0·37; and at 62·5°, 87·5° and 106°, equally, in 0·16 parts of water. (Brandes.) The solution has a light rose colour and thin syrupy consistence.

The salt dissolves readily in alcohol (John), but is insoluble in ether and in oil of turpentine. (Brandes.)

B. HYDROCHLORATE OF MANGANIC OXIDE.—Finely divided maganoso-manganic or manganic oxide—added by small portions at a time, in order to avoid rise of temperature—dissolves in cold concentrated aqueous hydrochloric acid, forming a brown solution, which slowly becomes colourless at ordinary temperatures, and more rapidly when heated or exposed to sunshine—chlorine being evolved and hydrochlorate of manganous oxide produced: hence the solution dissolves metals as readily as chlorine-water. It likewise converts sulphurous and hydrosulphuric acids into sulphuric, and tartaric into carbonic acid. The addition of water in large quantities precipitates manganic oxide, and gives rise to the formation of protochloride of manganese. (Forchhammer.)

C. *Terchloride of Manganese?*—Sulphuric acid is added to the green solution of mineral chameleon till the liquid turns red; after which it is evaporated to dryness,—and the residue, consisting of sulphate and permanganate of potash, is dissolved in oil of vitriol—the solution introduced into a tubulated retort—and fragments of fused chloride of sodium added as long as coloured vapours are evolved. The copper-coloured or green vapours which distil over, condense entirely in a tube attached to the retort, and cooled down to −15° or −20°, forming a greenish brown liquid. The vapours, when brought in contact with moist air in a wide tube, produce a dense, rose-coloured cloud, and form on the sides of the tube, with formation of hydrochloric acid, a deposit of purple-red permanganic acid. (Dumas, *Ann. Chim. Phys.* 36, 81; also, *Pogg.* 11, 165; also, *N. Tr.* 17, 1, 194.) This compound is probably analogous to chlorochromic acid. (H. Rose.)

D. CHLORATE OF MANGANOUS OXIDE.—Known only in solution. Colourless liquid.

E. PERCHLORATE OF MANGANOUS OXIDE, or MANGANOUS PERCHLORATE.—Sulphate of manganous oxide is precipitated by perchlorate of baryta in equivalent proportions—the mixture heated—and the filtrate left to evaporate in a dry warm place.—The salt separates in long needle-shaped crystals, which are highly deliquescent and soluble in alcohol. (Serullas, *Ann. Chim. Phys.* 46, 305.)

MANGANESE AND FLUORINE.

A. PROTOFLUORIDE OF MANGANESE.—Deposited on evaporating a solution prepared from carbonate of manganous oxide and aqueous hydrofluoric acid, in small, pale, amethyst-red, ill-defined crystals, or in the form of a powder of the same colour. Not decomposed at a red heat. Dissolves in water when it contains an excess of acid. (Berzelius; *see also*, Unverdorben, *N. Tr.* 9, 1, 24.)

B. SESQUIFLUORIDE OF MANGANESE.—The native hydrated sesquioxide, reduced to fine powder by levigation, is dissolved in aqueous hydrofluoric acid, and the deep red solution of acid sesquifluoride left to evaporate spontaneously. Crystallizes in dark brown prisms, which are slightly transparent, and ruby-coloured by transmitted light; the powder is also ruby-coloured. In small quantities of water it dissolves completely; but the solution, when diluted or boiled, deposits a *basic salt*, whilst an *acid salt* remains in solution. On cooling, a portion of the former is redissolved, if free acid is present in the liquid. Ammonia precipitates from the aqueous solution pure hydrated manganic oxide, free from all traces of hydrofluoric acid. (Berzelius.)

C. *Seven-halves Fluoride of Manganese?*—When a mixture of 2 parts of mineral chameleon, or crystallized permanganate of potash, and 1 part of fluorspar, is digested with oil of vitriol in a platinum retort, it evolves a yellow vapour (or gas), which changes to purple on coming in contact with the air, provided the air contains moisture. The yellow vapour corrodes glass, being resolved into fluoride of silicium and permanganic acid, which covers the glass in the form of a brown layer, and dissolves in water with a purple colour. Chloride of calcium exposed to the yellow vapour, becomes heated and evolves chlorine. The compound is absorbed by water, forming a purple solution, which contains hydrofluoric and permanganic acids. The solution remains unchanged in stoppered bottles, but, when evaporated, evolves oxygen gas and hydrofluoric acid vapour, and leaves a brown shining residue, from which water dissolves hydrofluate of manganous oxide, leaving a black, insoluble, basic salt. The solution also dissolves copper, mercury, and silver, (not gold or platinum,) forming salts of hydrofluoric acid, and at the same time becomes perfectly colourless. (Wöhler, *Pogg.* 9, 619; see also Dumas, *Ann. Chim. Phys.* 36, 82.)

Manganese and Nitrogen.

A. Nitrite of Manganous Oxide, or Manganous Nitrite.—Deliquescent. (Mitscherlich.)

B. Nitrate of Manganous Oxide, or Manganous Nitrate.—Manganese dissolves readily in nitric acid, with evolution of heat and nitric oxide gas; the peroxide dissolves in hot nitric acid, only when sugar or some other deoxidizing substance is present to convert the nitric into nitrous acid; or, according to Scheele, when the mixture is exposed to the sun's rays, whereby also the nitric acid is resolved into oxygen and nitrous acid. The salt crystallizes with difficulty in combination with water, forming white, longitudinally striated needles, which when heated, rapidly deliquesce, evolving nitric acid in a state of decomposition and leaving black oxide of manganese. They likewise deliquesce when exposed to the air, and are readily soluble in water and alcohol. (John.) The crystals contain 6 atoms of water. (Millon, *Compt. Rend.* 14, 905.)

C. Permanganate of Ammonia.—Permanganate of silver is decomposed by triturating it in a mortar with the exact proportion of sal-ammoniac required, and with water; the solution is then filtered, and evaporated to the crystallizing point. Crystalline system, the right prismatic. *Fig.* 53; $u : u = 102° 20'$; $i : i = 102°$. Readily decomposed by heat. The solution, if it does not contain an excess of ammonia, may be evaporated without decomposition. (Mitscherlich.)

D. Carbonate of Manganous Oxide and Ammonia.—*Manganoso-ammonic Carbonate.*—When a salt of manganous oxide is precipitated by potash or carbonate of potash, and carbonate of ammonia is added, the precipitated hydrate or carbonate of manganous oxide, is quickly redissolved, forming a solution which is white at first, but afterwards becomes brown and turbid. (Wittstein, *Repert.* 57, 30.)

E. Phosphate of Manganous Oxide and Ammonia, or *Manganoso-ammonic Phosphate.*—A mixture of aqueous protochloride of manganese, free hydrochloric acid, and phosphoric acid or phosphate of soda, is boiled in a flask, and then supersaturated with ammonia, and the flask immediately corked. The white hydrated phosphate of manganous oxide first separated, changes in a few minutes into pearly scales of the double salt, which is then collected on a filter and washed with water. If the air is not completely excluded, hydrated sesquioxide of manganese is also precipitated, and imparts a reddish hue to the double salt; if once formed, however, the compound remains unaltered in the air, and may be washed with water containing air.—White pearly scales, resembling the acetate of mercurous oxide. ¶ Heintz prepares it by dropping an excess of ordinary phosphate of soda into a cold solution of manganous oxide, containing sal-ammoniac and a small quantity of free ammonia. Between 110° and 120°, it loses nothing but hygroscopic moisture. ¶

	Calculation.		Otto.		Heintz.
NH^3	17·0	9·07	9·16	+3HO	24·51
$2MnO$	72·0	38·42	37·84		38·35
cPO^5	71·4	38·10	37·86		38·37
$3HO$	27·0	14·41	15·14		
$NH^4O,2MnO,cPO^5+2Aq.$	187·4	100·00	100·00		101·23

When heated, it evolves ammonia and water, and leaves 75·7 per cent. of white [di-pyro]phosphate of manganous oxide. It is decomposed, with evolution of ammonia, by a concentrated solution of potash, but not by ammonia or carbonate of potash.—Dissolves readily in dilute acids; from the solution, ammonia precipitates phosphate of manganous oxide, which, however, is soon reconverted into the double salt. It does not dissolve in water or alcohol, not even at a boiling heat. (Otto, *Schw.* 66, 288.)

F. Ammonio-sulphate of Manganous Oxide.—100 parts of anhydrous sulphate of manganous oxide very slowly absorb 43·68 parts of dry ammoniacal gas, and crumble to a white powder. This powder, if preserved in a sealed glass tube, becomes brownish white after a while.—Gives off part of its ammonia when exposed to the air, and the whole when ignited. When this salt is dissolved in water, hydrated manganous oxide separates from it. (H. Rose, *Pogg.* 20, 148.)

	Calculation.		H. Rose.
MnO,SO^3	76	69·09	69·60
$2NH^3$	34	30·91	30·40
MnO,SO^3+2NH^3	110	100·00	100·00

G. Sulphate of Manganous Oxide and Ammonia.—*Manganoso-ammonic Sulphate.*—Prepared by mixing sulphate of manganous oxide with sulphate of ammonia in solution, and evaporating to the crystallizing point. (John.) A mixture of manganous sulphate and sal-ammoniac likewise yields crystals of the double salt, hydrochlorate of manganous oxide and ammonia remaining in the mother-liquid. (A. Vogel, *J. Pr. Chem.* 1, 195.)—The compound forms pale rose-coloured transparent crystals, which, according to Mitscherlich, have the same form as the double sulphate of magnesia and ammonia. (*Fig.* 84.)—Between 75° and 87°, the crystals lose a portion of their water of crystallization; at a red heat, the whole of the water is driven off, together with the sulphate of ammonia. (A. Vogel.) They dissolve readily in water, and deliquesce in moist air. (John.) They are not precipitated by ammonia, if air be excluded.

	Calculation, according to Mitscherlich.	
NH^3	14	6·11
MnO	72	31·44
$2SO^3$	80	34·94
$7HO$	63	27·51
$NH^4O,SO^3+MnO,SO^3+6Aq.$	229	100·00

H. SULPHATE OF MANGANIC OXIDE AND AMMONIA.—*Mangano-ammonic Sulphate.—Ammonia Manganese-alum.*—Finely divided peroxide of manganese is gently heated with oil of vitriol, and the red solution mixed with sulphate of ammonia and left to crystallize. Dark red, regular octohedrons, which crystallize only from a very acid solution, and when dissolved in water, are decomposed, with separation of manganic oxide. (Mitscherlich.)

Calculation, according to Mitscherlich.

NH^3	17	3·53
Mn^2O^3	80	16·60
$4SO^3$	160	33·19
25HO	225	46·68
$NH^4O,SO^3 + Mn^2O^3,3SO^3 + 24Aq.$	482	100·00

I. HYDROCHLORATE OF MANGANOUS OXIDE and AMMONIA.—*Manganoso-ammonic Hydrochlorate.*—Prepared by mixing hydrochlorate of manganous oxide with sal-ammoniac.—Crystallizable.—Ammonia does not precipitate the aqueous solution, if air is perfectly excluded; on its admission, however, the liquid first becomes turbid and white, and then brown, and lastly deposits the manganese in the form of hydrated sesquioxide; the greater the excess of ammonia, the more complete is the precipitation. (Vid. Hatchett, *Schw.* 14, 352.) ¶ Prepared by Hautz (*Ann. Pharm.* 66, 286), by mixing 2 parts of protochloride of manganese with 1 part of sal-ammoniac in solution, and setting aside to crystallize.—Pale red salt, soluble in 1⅓ parts of water at ordinary temperatures, and having the same crystalline form as the magnesia-salt. ¶

The hydrate, carbonate, and phosphate of manganous oxide dissolve in a solution of sal-ammoniac. (Brett.) The solution yields a flesh-coloured precipitate with hydrosulphuric acid (Brett), and gradually becomes turbid when left to itself, that of the hydrated protoxide depositing a brown precipitate. (Wittstein.) The solution doubtless contains the above-mentioned double salt, together with caustic ammonia, or carbonate or phosphate of ammonia. The hydrate, carbonate, or phosphate of manganous oxide, behaves in a similar manner with sulphate or nitrate of ammonia.

MANGANESE AND POTASSIUM.

A. MANGANATE OF POTASH.—*Mineral Chameleon.*—Formed when any oxide of manganese is ignited with hydrate of potash, carbonate of potash, nitre, or a mixture of potash and chlorate of potash. In the two latter cases, the oxygen required for the formation of the manganic acid, is furnished by the nitre or the chlorate of potash; when the hydrate or carbonate is used, the oxygen is derived from the air; or if air is excluded, and peroxide of manganese used, one portion of that substance yields the required quantity of oxygen to another portion, and is itself reduced to the state of manganoso-manganic oxide. According to Chevillot & Edwards, a mixture of 44 parts of peroxide of manganese with four times its weight of hydrate of potash, ignited in oxygen gas, absorbs from 9·4 to 10·4 parts of oxygen, or rather more than one atom; probably, however, the peroxide of manganese used by those chemists was mixed with sesquioxide.—The green colour of potash or carbonate of potash, into which portions of ash fall during fusion, arises from the formation of manganate of potash.

Preparation.—One part of very finely pounded peroxide, or some other oxide of manganese, is ignited with 3 parts of nitre, or in an open vessel with 2 parts of hydrate or carbonate of potash, till a small portion of the mass taken out as a sample, and allowed to cool, dissolves almost wholly in water, forming a dark green solution. When nitre is used, the mixture becomes semi-fluid during ignition, and finally assumes a pasty consistence.—In this manner *Mineral Chameleon* (*Chamæleon minerale*) is obtained; it is a blackish green substance, which yields a dark green powder, and, besides manganate of potash, may contain manganic oxide, potash, and carbonate, and nitrite of potash.

To obtain the pure crystallized salt from this substance, it is dissolved in a small quantity of pure water, the solution decanted from sesquioxide of manganese, and evaporated in vacuo over oil of vitriol. It forms green crystals of precisely the same form as sulphate of potash. *Fig.* 76; $y : y' = 121° \; 10\frac{1}{2}'$; $y : h = 119° \; 24\frac{1}{2}'$. (Mitscherlich.)

	Crystallized.		Or:			Mitscherlich.
KO	47·2	47·58	3KO	141·6	47·58	46·34
MnO^3	52·0	52·42	Mn^3O^4	116·0	38·98	38·12
			5O	40·0	13·44	14·50
KO,MnO^3	99·2	100·00	$3(KO,MnO^3)$	297·6	100·00	98·96

The crystals, when boiled with a small quantity of dilute nitric acid, deposit hydrated peroxide of manganese and evolve 8·7 per cent. of oxygen. They are decomposed by water, yielding a red solution of permanganate of potash and a brown crystalline compound of peroxide of manganese and potash, which almost immediately gives up its potash to the water, and leaves pure hydrated peroxide of manganese. (Mitscherlich.)

$$3(KO,MnO^3) = KO,Mn^2O^7 + 2KO + MnO^2.$$

This decomposition appears to result from the affinity of water for potash, by which two-thirds of the alkali are removed from the salt. The crystals dissolve without decomposition in an aqueous solution of potash, forming a green solution, from which they are again separated, together with free potash, by evaporation in vacuo. But if the solution in potash is exposed to the air, it turns red from absorption of carbonic acid, and deposits insoluble peroxide of manganese. (Mitscherlich.) The mineral chameleon—inasmuch as it contains an excess of potash—forms with water a solution which is dark green at first, but rapidly changes through blue, violet, and purple to carmine-red, in proportion as the excess of potash is removed from the salt by the water—especially when it is added in large quantities or when it is hot—and by the carbonic acid of the air; for the same reason, also, sulphuric acid, nitric acid, carbonate of ammonia, &c. produce the red colour. (Chevillot & Edwards.) A solution of mineral chameleon in boiled water, even when kept in air-tight bottles completely filled with it, gradually turns red—showing that the affinity of the water for the potash is of itself sufficient to decompose the salt: a small quantity of peroxide of manganese is precipitated at the same time. (Fromherz.) Whether the green solution is reddened by spontaneous decomposition, or by the action of carbonic acid, nitric acid, &c., the change of colour is invariably accompanied by precipitation of peroxide of manganese. (Forchhammer.)

B. Permanganate of Potash.—1. One part of peroxide of manganese is ignited with one part of hydrate of potash (or 1·8 of nitre); the resulting mass dissolved in water; and the red solution decanted and evaporated, rapidly at first till small needles appear, and afterwards cautiously, so that the crystallization may go on regularly. (Chevillot & Edwards.)—2. Chlorate of potash being kept in a state of fusion over a spirit-lamp, hydrate of potash is first added to it, and then an excess of finely divided peroxide of manganese, which immediately dissolves, forming a splendid green solution. The mixture is then heated till the whole of the chlorate of potash is decomposed; and the mass when cold is boiled with a small quantity of water, whereupon the green colour of the solution changes to red; finally, the liquid is decanted from the peroxide of manganese while still hot, and set aside to crystallize by cooling. The mother-liquor of the permanganate of potash yields crystals of chloride of potassium, and if the chlorate of potash has not been completely decomposed, crystals of this salt are likewise obtained, of a beautiful red colour, arising from the presence of permanganate of potash. (Wöhler, *Pogg.* 27, 626.) Gregory (*J. Pharm.* 21, 312; also *Ann. Pharm.* 15, 237) adds to a finely divided mixture of 8 parts (3 atoms) of peroxide of manganese and 7 parts (1 atom) of chlorate of potash, a solution of 10 parts (3 atoms) of hydrate of potash in a very small quantity of water; evaporates to dryness, during which a small quantity of mineral chameleon is formed; ignites the finely pounded mass in a platinum crucible over a spirit-lamp, till the whole of the chlorate of potash is decomposed (for which a low red heat is quite sufficient); reduces the semi-fused mass to coarse powder; boils it in a larger quantity of water; allows the insoluble portion to subside and decants; evaporates the clear solution rapidly; again decants from the freshly precipitated peroxide of manganese; and leaves the solution to crystallize by cooling. The crystals are then washed with a small quantity of cold water; dissolved in the smallest possible quantity of boiling water; and the solution left to crystallize by cooling. In this manner, needles are obtained $\frac{3}{4}$ inch in length, and amounting in weight to about a third of the peroxide of manganese employed. If it be desired to filter the solution, in order to avoid the loss arising from decantation, a funnel may be used, having its neck filled with asbestos.

The salt crystallizes in dark purple needles, having first a sweet, and afterwards a rough taste; it does not redden turmeric, and is permanent in the air. (Chevillot & Edwards.) It belongs to the right prismatic system of crystallization. *Fig.* 53, $u : u' = 103° 1\frac{1}{2}'$; $i : i = 101° 40\frac{1}{3}'$. (Mitscherlich.)

	Calculation.		Mitscherlich.	Unverdorben.
KO	47·2	29·65	30·385	25·63
Mn^2O^7	112·0	70·35	69·580	
KO,Mn^2O^7	159·2	100·00	99·965	

The crystals decrepitate when heated, evolving 10·8 per cent. of oxygen gas, and are converted into a black powder from which water extracts manganate of potash, and leaves 54 per cent. of black manganic oxide. When heated in an atmosphere of hydrogen gas, they become red-hot and diminish in bulk, at first rapidly, afterwards slowly, with formation of a green mixture of hydrate of potash and protoxide of manganese. One gramme of the crystals absorbs in this process 35·55 centilitres of hydrogen gas (or 1 grain absorbs 1 cubic inch). The crystals detonate when rubbed up with phosphorus, and the violence of the detonation is increased by heat; they also detonate with sulphur, but less powerfully, and only partially by trituration. A mixture of the crystals with charcoal does not take fire when rubbed in a mortar, but when heated it burns like tinder; they likewise detonate with arsenic and inflame with antimony on the application of heat. Lycopodium mixed with the salt takes fire on the addition of oil of vitriol. The crystals dissolve in oil of vitriol without effervescence, forming an olive-green solution; in this solution, decomposition takes place very slowly; the addition of a small quantity of water changes its colour to light green; a larger quantity to orange yellow; and a still larger quantity to scarlet. An aqueous solution of phosphoric acid, of specific gravity 1·80, likewise dissolves the crystals slowly, forming also a green solution. The other mineral acids, whose specific gravity is lower, and sulphuric acid when reduced to the density of 1·60, produce a red solution, which, in various lengths of time (in a few hours with concentrated nitric acid, and after some months with dilute nitric acid) gives off oxygen gas, with effervescence, and deposits a brown flocculent precipitate, the liquid itself becoming colourless. (Chevillot & Edwards.) An aqueous solution of the salt mixed with nitric or sulphuric acid, evolves bubbles of oxygen gas, slowly at a temperature of 30°, but rapidly when boiled, hydrated peroxide of manganese being at the same time precipitated. (Mitscherlich.)

The crystals dissolve in 16 parts of water at 15°. (Mitscherlich.) The light purple colour of this solution changes, through violet and blue, to green on the addition of potash; a large quantity of the alkali is however necessary, unless the mixture is continually shaken; and the quantity required is greater, the more dilute the solution and the higher the temperature. A green solution turned red by boiling, continues red on cooling, but recovers its green colour when shaken; a green solution when evaporated turns red, in consequence of the elevation of temperature, and then green again, from loss of water; the last-mentioned green solution sometimes yields red crystals. (Chevillot & Edwards.) Perfectly pure potash does not change the colour of the red solution to green, except on the addition of a minute quantity of alcohol; a larger proportion of alcohol decolorizes the solution and precipitates peroxide of manganese. Carbonate of manganous oxide, suspended in solution of potash, likewise changes the red solution to green, and is itself converted into a salt of manganic oxide. (Forchhammer.) If the red crystals are dissolved in solution of potash, and the solution left to evaporate in vacuo, red crystals are again obtained, a small portion only being decomposed. But a very dilute solution of the salt in caustic potash slowly becomes green at ordinary temperatures, and more quickly when heated. In order that the red salt may be completely changed into the green, the quantity of the aqueous solution must be sufficient to absorb the oxygen gas set free by the conversion of the permanganic into manganic acid. The green solution is again reddened by acids, with separation of hydrated peroxide of manganese. (Mitscherlich.) The red solution of the crystals is also turned green by solution of soda, by baryta, and strontia-water, and even by lime-water; in the last case, however, the effect is but slight, in consequence of the great dilution of the liquid. In these cases, double salts of manganic acid appear to be formed, inasmuch as manganate of baryta, for instance, is not soluble in water by itself, and nevertheless no precipitation takes place. (Chevillot & Edwards.) The red aqueous solution may be preserved unchanged if kept from the action of deoxidizing substances; in the contrary case, the manganic acid loses oxygen and is precipitated as hydrated [per]oxide in brown flakes, the solution at the same time becoming colourless, and, if deoxidized by organic substances, saturated with carbonic acid. (Chevillot & Edwards.) Sulphurous acid gives rise to the formation of sulphuric acid and protoxide of manganese. (Chevillot & Edwards.) Hydrosulphuric acid in excess decolorizes the solution, precipitating pale red hydrosulphate of manganous oxide, and forming sulphurous acid. Ammonia evolves nitrogen gas and precipitates hydrated peroxide of manganese. Nitric oxide throws down hydrated peroxide of manganese and forms nitrate of potash. Arsenious acid colours the solution brown or brownish-yellow, according to its degree of dilution, and after some time decolorizes it, throwing down a brown precipitate. Arsenite of potash, according to Bonnet (*Pogg.* 37, 303), precipitates a brown oxide of manganese. Mercury also decolorizes the solution, itself becoming oxidized. (Chevillot & Edwards.) All organic substances exert a deoxidizing action on the solution. Alcohol acts with peculiar rapidity; gum, sugar, paper (*e.g.* when used to filter the solution) act more slowly. Decolorization also takes place when the liquid is exposed in open vessels, organic particles falling into it from the air, and carbonic acid, at the same time combining with the potash. Hydrate of potash purified by alcohol, and consequently containing organic matter, and carbonate of soda which has been frequently filtered through paper, likewise act as deoxidizing agents. (Chevillot & Edwards.)—Tartaric or racemic acid, supersaturated with potash, rapidly decolorizes the solution, first, however, imparting to it a transient green colour; citric acid supersaturated with potash, slowly changes the red solution to green, which latter colour remains permanent for a considerable time. (H. Rose, *Pogg.* 59, 320.)

Permanganate of potash crystallizes in all proportions with perchlorate of potash, with which it is isomorphous; the latter salt crystallizes in splendid red crystals, when a small quantity of permanganate of potash is added to its solution. With equal parts of the two salts, the crystals are nearly black. (Wöhler.)

¶ C. SULPHIDE OF MANGANESE AND POTASSIUM. $3MnS + KS$.—1. Prepared by fusing anhydrous sulphate of manganous oxide with $\frac{1}{5}$ of its weight of lamp-black, and 3 times its weight of carbonate of potash and sulphur. A gentle heat is applied at first, till the carbonic acid is expelled and the sulphide of potassium formed; afterwards the heat is raised to bright redness. On cooling, a perfectly fused mass is obtained, which, after the excess of sulphide of potassium has been removed by cold boiled water, leaves large dark red scales collected together in masses; these masses may be readily split, like mica, into thin, transparent, dark-red laminæ.—2. By substituting peroxide of manganese for the manganous sulphate, a similar compound is obtained, but of less brilliant colour.—The scales, when moist, are rapidly oxidized in the air, becoming black and opaque, but, when perfectly dry, they remain permanent for a considerable time. They are nearly insoluble in water, alcohol, and ether. They detonate violently with nitre. Acids dissolve them, with rapid evolution of hydrosulphuric acid gas. When heated on platinum wire, they become covered with a green powder of oxysulphide of manganese. They are gradually resolved by water containing air, into sulphate of potash, sulphide of potassium, and manganous hyposulphite, which dissolve, and an insoluble mixture of sulphur and manganic oxide. (Völker.) ¶

	Calculation.		Völker.
3Mn	84·0	44·46	44·74
K	39·2	21·02	20·48
4S	64·0	34·52	33·09
3MnS + KS	187·2	100·00	98·31

D. Sulphate of Manganous Oxide and Potash.—*Manganoso-potassic Sulphate.*—Pale red crystals having the form of sulphate of magnesia and ammonia. (*Fig.* 84.) (Mitscherlich.)

Calculation, according to Mitscherlich.		
KO	47·2	21·73
MnO	36·0	16·57
$2SO^3$	80·0	36·84
6HO	54·0	24·86
$KO, SO^3 + MnO, SO^3 + 6Aq.$	217·2	100·00

E. Sulphate of Manganic Oxide and Potash, or *Manganous-potassic Sulphate.*—*Potash Manganese-alum.*—A mixture of manganic sulphate in excess, with a saturated solution of sulphate of potash, is evaporated at a gentle heat to a syrupy consistence, and then left to cool slowly; dark violet-coloured regular octohedrons are then deposited. The salt is decomposed when redissolved in water, and on evaporating the solution, sulphate of potash alone crystallizes out. (Mitscherlich.)

Calculation, according to Mitscherlich.		
KO	47·2	9·38
Mn^2O^3	80·0	15·90
$4SO^3$	160·0	31·79
24HO	216·0	42·93
$KO, SO^3 + Mn^2O^3, 3SO^3 + 24Aq.$	503·2	100·00

F. Fluoride of Manganese and Potassium.—Manganous sulphate precipitated by fluoride of potassium, yields a white precipitate, which is insoluble in water, but dissolves with tolerable facility in acids (Gay-Lussac & Thenard); according to Berzelius, this precipitate is a compound of fluoride of potassium with fluoride of manganese.

Manganese and Sodium.

A. Manganate of Soda.—On igniting peroxide of manganese with an equal weight of hydrate of soda, oxygen gas is absorbed, and a blackish mass produced, which dissolves in water, forming a green solution which rapidly changes to red. (Chevillot & Edwards.)—This salt is so very soluble in water, that it cannot be purified by crystallization. (Mitscherlich.)

Before the blowpipe, carbonate of soda fuses with manganic oxide on platinum foil or platinum wire, forming a dark bluish green mass; one part of manganic oxide is sufficient to impart a distinct green colour to 1000 parts of carbonate of soda. (Berzelius.)

B. Permanganate of Soda.—Formed in the aqueous solution of manganate of soda; it does not yield distinct crystals when evaporated. (Chevillot & Edwards.)—Deliquescent. (Mitscherlich.)

C. and D. The oxides of manganese dissolve in fused *borax*, forming a dark amethyst-red glass, which becomes colourless in the inner flame.—They behave in a similar manner with *microcosmic salt*, excepting that the glass so formed is of a less intense colour, and more readily decolorized in the inner flame. Nitre immediately restores the red tint to the colourless glass formed in the inner flame. (Berzelius.)

E. SULPHIDE OF MANGANESE AND SODIUM.—1. A mixture of 10 parts of ignited manganous sulphate with 5 parts of fused Glauber's salts, heated to whiteness in a charcoal crucible, yields 7·8 parts of a compound which contains 26 per cent. of sulphide of sodium, and has a light brownish-red colour, without metallic lustre; it is dense, has a granular fracture, and fuses at 60° Wedgewood. (Berthier, *Ann. Chim. Phys.* 22, 247.) ¶ 2. Obtained in a similar manner to the potassium compound.—Small, shining, light-red needle-shaped crystals, resembling those of sulphide of manganese and potassium in most of their properties, but more readily oxidable. When treated with distilled water, they rapidly become opaque and dark-coloured. If in this state they are placed over oil of vitriol in vacuo, they rapidly absorb oxygen as soon as they become moderately dry; and the absorption is attended with so violent a disengagement of heat, that the crystals frequently take fire and burn like a pyrophorus. (Vőlker.)

	Calculation.				Völker.
3Mn	84·0	...	48·6	......	49·11
Na	23·2	...	13·6	......	13·26
4S	64·0	...	37·8	......	37·18
3MnS + NaS	171·2	...	100·0	......	99·55 ¶

F. SULPHATE OF MANGANOUS OXIDE AND SODA.—*Manganoso-sodic Sulphate.*—If the residue obtained in the preparation of chlorine from peroxide of manganese, common salt, and sulphuric acid is ignited, and afterwards dissolved in water, and the solution evaporated, crystals of sulphate of soda are obtained. The mother-liquid decanted from these crystals, if left in a cool place for a year, deposits crystals of the salt β; and the mother-liquor then remaining, yields, on further standing, large crystals of the salt α.

α. *Bi-hydrated.*—Obtained by the above method, or, according to Arrott (*Ann. Pharm.* 52, 243), by evaporating a solution of the two salts in equivalent proportions, at a temperature of 50°.—Crystallizes in transparent, light yellow, oblique rhombic prisms, with the acute lateral edges truncated.—Not efflorescent.

NaO	31·2	...	18·88
MnO	36·0	...	21·79
$2SO^3$	80·0	...	48·43
2HO	18·0	...	10·90
$NaO, SO^3 + MnO, SO^3 + 2Aq.$	165·2	...	100·00

Or:					Geiger.
NaO, SO^3	71·2	..	43·1	......	42·00
MnO, SO^3	76·0	...	46·0	......	44·17
2HO	18·0	...	10·9	......	10·83
	165·2	...	100·0	......	97·00

β. *Sexhydrated.*—Crystallizes in transparent, pale rose-coloured oblique rhombic prisms, often having their summits and lateral edges truncated. [The similarity of the crystalline form would lead to the supposition that this salt is isomorphous with the sulphate of manganous oxide and potash, and, like that salt, contains not 5, as Geiger asserts, but 6 atoms of water; the salt examined by Geiger, as he himself observed, was mixed with the salt α.]—This salt reddens litmus slightly, and has at first a cooling, bitterish, and afterwards an unpleasant, strongly metallic taste. It effloresces in a warm atmosphere, with the exception of any crystals of salt α that may be enclosed within it. —Decrepitates slightly when heated, swells up to a white porous mass, and, at a low red heat, fuses to a whitish grey mass, which is still perfectly soluble in water. If the ignition be carried beyond a certain point, a portion of manganoso-manganic oxide is left on dissolving the residue in water.

	Calculation.		Geiger.
NaO	31·2	16·23	17·0
MnO	36·0	18·73	19·0
$2SO^3$	80·0	41·62	42·5
5HO	45·0	23·42	21·0
$NaO,SO^3 + MnO,SO^3 + 5Aq.$	192·2	100·00	99·5

	Probably more nearly.	
NaO	31·2	15·51
MnO	36·0	17·89
$2SO^3$	80·0	39·76
6HO	54·0	26·84
$+ 6Aq.$	201·2	100·00

The salt β dissolves in 1·2 parts of boiling water, and the solution deposits nothing on cooling, either in covered or open vessels, or on being shaken; but if, after twenty-four hours, a crystal of the same salt is introduced into the solution, there is deposited, in about three hours, a thickish mass, which, when pressed, is resolved into crystallized sulphate of soda, and a mother-liquid which holds manganous sulphate in solution. The salts α and β both deliquesce in moist air. (Geiger, *Mag. Pharm.* 11, 27.)

G. Fluoride of Manganese and Sodium.—This compound dissolves with difficulty in water. (Berzelius.)

H. Pyrophosphate of Manganous Oxide, Soda, and Ammonia. —When ignited phosphate of soda is dissolved in water, and the solution mixed with manganous phosphate and free ammonia, a flocculent precipitate is formed, which rapidly changes into a yellowish white crystalline powder; the precipitate must be washed with cold boiled water. The powder is permanent in the air, evolves water and ammonia when heated, and leaves a greyish white, pasty, fused mass, the solution of which reddens litmus. A concentrated solution of potash decomposes the salt with evolution of ammoniacal gas; when boiled with strong nitric acid, it deposits peroxide of manganese, and on evaporation yields red prisms, probably consisting of permanganate of soda [or phosphate of manganic oxide?] It is insoluble in water and alcohol, but dissolves readily in acids, even when dilute. (Otto, *J. Pr. Chem.* 2, 418.)

	Calculation.		Otto.
NH^3	17·0	5·21	4·90
NaO	31·2	9·57	7·90
$2MnO$	72·0	22·09	22·37
$2bPO^5$	142·8	43·80	44·37
$7HO$	63·0	19·33	20·46
$NH^4O,MnO,bPO^5+NaO,MnO,bPO^5+6Aq.$	326·0	100·00	100·00

Manganese and Lithium.

Permanganate of Lithia.—Crystallizable. (Mitscherlich.)

Manganese and Barium.

A. **Manganate of Baryta.**—1. Peroxide of manganese, intensely ignited with an equal weight of baryta, absorbs oxygen, and yields a dark grey mass, insoluble in water. (Chevillot & Edwards.)—2. A mixture of peroxide of manganese and carbonate of baryta, exposed to the strongest heat of a blast-furnace, yields a crystalline mass, in the fissures of which small four-sided prisms are found. (Abich, *Pogg.* 23, 338.)—3. By igniting peroxide of manganese with nitrate of baryta, and washing the resulting mass with boiling water, an emerald-green powder is obtained, which, when dry, is permanent in the air. (Forchhammer.)—The manganate of baryta, prepared by igniting one part of peroxide of manganese with 2 parts of nitrate of baryta, is of a pale green colour, (Fromherz.)—4. When hydrate of baryta is dissolved in fused chlorate of potash, finely divided peroxide of manganese then added, and the resulting mass cooled, pounded, and exhausted by boiling in water, manganate of baryta remains behind in the form of a powder having a fine green colour. (Wöhler, *Pogg.* 27, 628.)—5. An aqueous solution of permanganic acid, mixed with baryta-water in excess, deposits, after a short time, a bluish green powder. (Fromherz.) When baryta-water is added to an aqueous solution of permanganate of baryta, and the mixture left to stand in a vessel half filled with it, green insoluble crystals of manganate of baryta are formed on the surface. (Mitscherlich.)

B. **Permanganate of Baryta.**—Permanganate of potash is not decomposed by chloride of barium. (Mitscherlich.)—Manganate of baryta diffused in water is decomposed by a current of carbonic acid gas, and the solution filtered and evaporated to the crystallizing point. (Fromherz, Wöhler, Mitscherlich.)—This salt crystallizes in nearly black needles, which are permanent in the air, and have exactly the primary and secondary forms and the angles of anhydrous sulphate or seleniate of soda. (Mitscherlich.) The red solution yields with a small quantity of baryta-water, a violet-coloured liquid, which loses its alkaline reaction after a while, and when evaporated, even at a temperature below 50°, deposits green manganate of baryta. (Fromherz.)—An aqueous solution of permanganate of potash yields, with baryta-water, a violet-coloured mixture, which afterwards becomes colourless, and deposits a blue precipitate. This precipitate retains its colour after washing and drying, and when decomposed by dilute sulphuric acid, yields aqueous permanganic acid and a precipitate of hydrated peroxide of manganese. The blue colour appears to indicate the presence of a mixture of manganate and permanganate of baryta. (Gmelin.)

MANGANESE AND STRONTIUM.

A. MANGANATE OF STRONTIA.—1. Prepared by strongly igniting a mixture of equal weights of peroxide of manganese and strontia. Pale green mass, insoluble in water. (Chevillot & Edwards.)—2. Fromherz ignites one part of peroxide of manganese with two parts of nitrate of strontia.

B. PERMANGANATE OF STRONTIA. — Deliquescent. (Mitscherlich.) When an excess of strontia-water is added to an aqueous solution of permanganic acid, the violet colour of the liquid gradually changes to pale green, without the formation of a precipitate: if a smaller quantity of strontia-water is used, the solution retains its violet colour and soon exhibits a neutral reaction. (Fromherz.)

MANGANESE AND CALCIUM.

Lime and nitrate of lime, when ignited with peroxide of manganese, have as little tendency as the earths to form a salt of manganic acid. (Chevillot & Edwards, Forchhammer, Fromherz.)

PERMANGANATE OF LIME.—Deliquescent. (Mitscherlich.)

MANGANESE AND MAGNESIUM.

PERMANGANATE OF MAGNESIA.—Deliquescent. (Mitscherlich.)

MANGANESE AND ALUMINUM.

SULPHATE OF ALUMINA AND MANGANOUS OXIDE.—Occurs in the hydrated state in asbestos-like masses, consisting of transparent, silky fibres. In taste and solubility it resembles common alum, but does not appear to crystallize in octohedrons. (Apjohn, Kane, *Pogg.* 44, 471.)

	Calculation.		Apjohn.	Kane.
MnO	36·0	7·62	7·33	
Al^2O^3	51·4	10·88	10·65	
$4SO^3$	160·0	33·87	32·79	
25HO	225·0	47·63	48·15	47·6
MgO,SO^3			1·08	
	472·4	100·00	100·00	

$(MnO,HO,SO^3) + (Al^2O^3,3SO^3) + 24Aq.$—MnO,HO replaces KO in potash-alum, or NH^4O in ammonia-alum. (Kane.)

MANGANESE AND SILICIUM.

A. SILICATE OF MANGANOUS OXIDE, OF MANGANOUS SILICATE.—*a. Disilicate.*—*a. Anhydrous.*—When 2 atoms of manganous oxide are fused with one atom of silica, crystals are obtained, agreeing with those of chrysolite. (Berthier, *Ann. Chim. Phys.* 24, 355.) The ore from Franklin in New Jersey, examined by Thomson, and Breithaupt's *Thephroite*, which, according to Rammelsberg, forms a stiff jelly with hydrochloric acid, both belong to this head.

	Calculation.		Thomson.		Rammelsberg. *Thephroite.*
$2MnO$	72	69·9	66·60		68·88
SiO^2	31	30·1	29·64		28·66
Fe^2O^3			0·92	FeO	2·92
HO			2·70	CaO,MgO	traces
$2MnO,SiO^2$	103	100·0	99·86		100·46

β. Hydrated.—Hydrosilicate of Manganese, (Schwarzer Mangan-kiesel.) —Amorphous, soft, iron-black substance. When heated, it evolves water, and becomes lighter in colour. At a higher temperature, it increases in bulk and becomes still lighter. Fuses in the outer blowpipe flame to a black, and in the inner flame to a green glass. (Berzelius.) Dissolves readily in acids, with separation of silica.

	Calculation.		Klaproth. Klapperud.
$2MnO$	72	59·50	55·8
SiO^2	31	25·62	25·0
$2HO$	18	14·88	13·0
$2MnO,SiO^2 + 2Aq.$	121	100·00	93·8

b. Monosilicate.—Siliciferous Manganese, Red Manganese, Rother Mangankiesel, Rothbraunsteinerz.—This mineral has two planes of cleavage, which intersect each other at angles of 92° 55′ and 87° 5′; it is probably isomorphous with Augite; specific gravity from 3·5 to 3·6, hardness equal to that of Apatite. Translucent and rose-coloured. Before the blowpipe in the inner flame, it yields a turbid rose-coloured glass, and in the outer flame a black bead, having a metallic lustre. (Berzelius.)

	At.			Berzelius. *a.*	At.			Dumas. *b.*
CaO				3·12	1	28	14·51	14·57
MgO				0·22				FeO 0·81
MnO	1	36	53·73	49·04	2	72	37·30	36·06
SiO^2	1	31	46·27	48·00	3	93	48·19	48·90
MnO,SiO^3	1	67	100·00	100·38	1	193	100·00	100·34

In the *Siliciferous Manganese* (*a*) from Longsbanshyttan, a small quantity of protoxide of manganese is replaced by lime; in the *Bustamite* (*b*) from Mexico, to the amount of one-third. To this class also appears to belong Thomson's bisilicate of manganese, in which the protoxide of manganese is partially replaced by protoxide of iron.

If one atom of SiO^2 is fused in a charcoal crucible with 2 atoms of MnO, in a powerful blast-furnace, a great part of the manganese is reduced, and after fusing ¾ of an hour, a hyacinth-red glass is obtained, composed of 62·1 parts of manganous oxide and 37·9 parts of silicic acid ($= 3MnO,2SiO^2$ nearly). At a still higher temperature, a larger portion of the manganese is reduced, and a pea-yellow coloured slag remains, in which 48·5 parts of manganous oxide are combined with 51·5 parts of silica ($= 4MnO,5SiO^2$ nearly). A mixture of MnO with SiO^2, when heated in a charcoal crucible, likewise yields reduced manganese, together with a pea-yellow coloured slag; but with the proportion of $2MnO$ to $3SiO^2$, a porous pea-yellow mass is obtained, without any reduction of manganese. (Sefström, *J. techn. Chem.* 10, 183.)

c. Tetrasilicate.—An aqueous solution of tetrasilicate of soda gives a white precipitate with sulphate of manganous oxide. (Walcker.)

B. SILICATE OF MANGANIC OXIDE, or MANGANIC SILICATE.—*a. Trisilicate.*—*Heteterocline.*—Oblique rhombic prisms of specific gravity 4·562; colour between iron-black and steel-grey; powder brownish-black.

	At.			Ewreinoff. St. Marcel.
KO				0·44
CaO				0·60
Mn^2O^3	3	240	88·56	85·88
Fe^2O^3				3·05
SiO^2	1	31	11·44	10·02
	1	271	100·00	99·99

b. Disilicate.—To this head belong the manganese ore from St. Marcel, analysed by Berzelius, and the *Siliciferous Manganese of Tinzen.* The latter is dense, with a granular and somewhat laminated fracture; hard, black, with faint metallic lustre, and yields a dark brown powder. When gently heated it loses water, and at a higher temperature gives off oxygen gas. Dissolves in warm hydrochloric acid, with evolution of chlorine and formation of a siliceous jelly. Sulphurous acid acts on it only with the aid of heat, and decomposes it completely, though with considerable difficulty; an aqueous solution of oxalic acid decomposes the fine powder completely when boiled with it for an hour.

	At.			Berzelius. St. Marcel.
Mn^2O^3	18	1440·0	76·60	75·80
Fe^2O^3	1	78·4	4·17	4·14
Al^2O^3	1	51·4	2·74	2·80
SiO^3	10	310·0	16·49	15·17
	1	1879·8	100·00	97·91

	At.			Schweizer. Tinzen.	Berthier.
CaO				1·70	
Mn^2O^3	19	1520·0	79·65	76·35	77·8
Fe^2O^3	1	78·2	4·10	3·70	1·0
Al^2O^3				trace	1·0
SiO^2	10	310·0	16·25	15·50	15·4
HO				2·75	2·8*
	1	1908·2	100·00	100·00	98·0

* The 2·8 per cent. in Berthier's analysis consists of quartz.

C. HYDROFLUATE OF SILICA AND MANGANOUS OXIDE.—$MnF, SiF^2 + 7Aq.$—Crystallizes from a highly concentrated solution, in long, regular, six-sided prisms,— or by slow evaporation, in shorter prisms and rhombohedrons. Colour very light red. When distilled, it first gives off 7 atoms of water and then gaseous fluoride of silicium, leaving fluoride of manganese of the same form as the original crystals. Easily soluble in water. (Berzelius.)

D. With glass-fluxes, manganous oxide yields colourless or pale red glasses; manganic oxide yields violet-red glasses.

E. Silicate of Glucina and Manganous Oxide.—Found native, containing sulphide of manganese, in the form of *Helvine.* Tetrahedrons. *Figs.* 13 & 14. Sp. gr. = 3·1. Harder than apatite. Translucent; yellow, with a tinge of green or brown. In the inner blowpipe flame, it fuses with ebullition, and forms a turbid yellow bead; in the outer flame it fuses with greater difficulty, and acquires a deeper colour. Dissolves slowly in borax, forming a clear glass, which, till the whole of the substance is dissolved, has a yellowish tinge arising from the presence of sulphide of sodium; but after the solution is complete, it appears colourless in the inner flame, and amethyst-red in the outer. Dissolves more readily in microcosmic salt, but with separation of a skeleton of silica, and yields a colourless glass which becomes opalescent on cooling. With carbonate of soda it first swells up, and then fuses to a black bead, which becomes brown in the inner flame; with carbonate of soda on platinum, after long blowing, it yields mineral chameleon. (Berzelius.) Dissolves in hydrochloric acid with evolution of sulphuretted hydrogen gas and separation of gelatinous silica.

	At.			C. Gmelin.
GO	3	38·1	13·46	12·03
MnO	3	108·0	38·15	31·82
FeO				5·56
SiO^2	3	93·0	32·85	33·25
MnS	1	44·0	15·54	14·00
HO				1·16
	1	283·1	100·00	97·82

The glucina is mixed with a small quantity of alumina.—$3(GO,MnO,SiO^2)+MnS$.

F. Silicate of Alumina and Manganous Oxide.—*Hydrated.*—*Karpholite.*—Fibrous; of specific gravity 2·93; harder than felspar; opaque; straw-yellow. When heated it gives off water and afterwards hydrofluoric acid; swells up before the blowpipe, and fuses with difficulty to a turbid brownish glass, which becomes darker in the outer flame. (Berzelius.) Scarcely attacked by hydrochloric acid.

	At.			Stromeyer.	Steinmann.
CaO				0·27	
MnO	1	36·0	21·51	19·16	17·09
Fe^2O^3				2·29	FeO 5·64
Al^2O^3	1	51·4	30·70	28·67	26·48
SiO^2	2	62·0	37·04	36·16	37·53
HO	2	18·0	10·75	10·78	11·36
F—O				1·47	
	1	167·4	100·00	98·80	98·10

Manganese and Titanium.

Titanate of Manganous Oxide, or Manganous Titanate.—*Greenovite.*—Crystalline system, the doubly oblique prismatic. *Fig.* 121, with three angles truncated, as well as the edges between *y* and *u*, and between

y and v; $y : u = 87° 10'$; $y : v = 85° 50'$; $u : v = 110° 35'$. Sp. gr. = 3·84; harder than felspar; dark rose-coloured. Infusible before the blowpipe; insoluble in hydrochloric acid; disintegrated by fused bisulphate of potash. Contains 24·8 per cent. of manganous oxide, 74·5 of titanic acid, and a trace of lime. (Dufrenoy.) Isomorphous with brown titanite; has two planes of cleavage, which intersect each other at an angle of 126° 56'. Specific gravity = 3·527. (Breithaupt.) Contains silica as an essential ingredient (Plattner); it is therefore *Titanite* in which the lime is replaced by protoxide of manganese. (Breithaupt.)

MANGANESE AND TANTALUM.

TANTALIDE OF MANGANESE.—Prepared by igniting a mixture of the two oxides in a charcoal crucible. Hydrochloric acid separates the manganese, and leaves the tantalum in the form of an insoluble black powder. (Berzelius.)

MANGANESE AND TUNGSTEN.

A. TUNGSTATE OF MANGANOUS OXIDE, or MANGANOUS TUNGSTATE.—*a. Monotungstate.*—Monotungstate of soda added to a neutral salt of manganous oxide throws down a greyish-white powder, which when heated becomes pale yellow, and loses water; at a higher temperature, the whole of the water is expelled, and the salt obtained in the fluid state. The hydrated powder gives up the whole of its tungstic acid to potash; it dissolves also in warm phosphoric or oxalic acid, sparingly in boiling acetic acid, and is insoluble in cold hydrochloric acid. (Anthon.)

	Ignited.		Anthon.		*Unignited.*		Anthon.
MnO	36	23·08	24·72	MnO	36	20·69	22
WO^3	120	76·92	75·28	WO^3	120	68·96	67
				2HO	18	10·35	11
MnO,WO^3	156	100·00	100·00	+2Aq.	174	100·00	100

b. Bitungstate.—Alkaline bitungstates precipitate from salts of manganous oxide, a white powder which turns yellow and loses water when ignited, and is soluble in aqueous phosphoric, oxalic, and nitric acid; the latter solution is rendered turbid by boiling, from separation of yellow tungstic acid. (Anthon, *J. pr. Chem.* 9, 339.)

	Ignited.		Anthon.		*Unignited.*		Anthon.
MnO	36	13·04	13·19	MnO	36	11·88	12
$2WO^3$	240	86·96	86·81	$2WO^3$	240	79·21	79
				3HO	27	8·91	9
$MnO,2WO^3$	276	100·00	100·00	+3Aq.	303	100·00	100

B. SULPHOTUNGSTATE OF MANGANESE.—MnS, WS^3. — Dissolves in water, forming a yellow solution. (Berzelius.)

MANGANESE AND MOLYBDENUM.

A. MOLYBDATE OF MANGANOUS OXIDE.—Molybdate of potash produces in a solution of protochloride of manganese, a brownish-white precipitate which is soluble in 40 or 50 parts of water. (Richter.)

B. SULPHOMOLYBDATE OF MANGANESE.—*a. With excess of Sulphide of Manganese.*—A solution of *b*, or a mixture of a manganous salt and of sulphomolybdate of potassium dissolved in water is precipitated by ammonia. The precipitate is a dark red powder, which becomes browner on drying. It is further decomposed by an excess of ammonia, whereupon it blackens from oxidation.

b. In equal numbers of atoms.—Formed by digesting in water a mixture of tersulphide of molybdenum and hydrated sulphide of manganese, the latter being in excess. The brownish-yellow solution obtained dries up to a transparent uncrystallizable varnish. The same compound is formed, but without precipitation, when a manganous salt is mixed with an aqueous solution of sulphomolybdate of potassium.

c. With excess of Tersulphide of Molybdenum.—Produced in the form of an insoluble compound, on digesting sulphide of manganese with excess of tersulphide of molybdenum. (Berzelius.)

C. PERSULPHOMOLYBDATE OF MANGANESE.—Prepared by precipitating a manganous salt with an aqueous solution of persulphomolybdate of potassium. Red powder. (Berzelius.)

MANGANESE AND VANADIUM.

A. VANADITE OF MANGANOUS OXIDE, OR MANGANOUS VANADITE.—Prepared by double decomposition. Brown. When exposed to the action of air under water, it assumes a yellow colour, and gradually disappears, while black crystals of manganous vanadiate are deposited. (Berzelius.)

B. VANADIATE OF MANGANOUS OXIDE, OR MANGANOUS VANADIATE.—*a. Monovanadiate.*—The yellow aqueous mixture of vanadiate of ammonia and protochloride of manganese in excess is precipitated by alcohol, and the rusty yellow precipitate washed with the same liquid; it is then dissolved in water and the solution left to evaporate spontaneously. The salt separates in small brownish black crystals, which yield a red powder, and are sparingly soluble in cold water, forming a yellow solution, from which they are again precipitated by alcohol.—*b. Bivanadiate.*—Crystallizes from an aqueous solution by spontaneous evaporation, in small red granules. Forms a yellow solution in water, and is again precipitated by alcohol in the form of a yellow powder. Dissolves with difficulty in cold water, forming a yellow solution. (Berzelius.)

MANGANESE AND CHROMIUM.

A. CHROMIDE OF MANGANESE.—1. A mixture of equal parts of sesquioxide of chromium and protoxide of manganese exposed to the heat of a blast-furnace in a charcoal crucible, yields an alloy which is permanent in the air, insoluble both in hydrochloric and in nitric acid, and dissolves only after prolonged boiling in aqua-regia. (Bachmann.)

B. CHROMATE OF MANGANOUS OXIDE, OR MANGANOUS CHROMATE.—*a. Dichromate.*—Manganous salts are coloured yellowish brown by monochromate of potash, and yield, after some time, a dark brown precipitate, which is deposited partly on the sides of the vessel and partly as a pellicle on the liquid. If the solution is largely diluted, the deposit has a crystalline aspect. Under the microscope, the formation of reddish-brown granules is first observed: these go on increasing in size, and afterwards fine needles are formed, which appear dark chocolate-brown by reflected, and deep brownish-red by transmitted light. The precipitate gives up its chromic acid to a boiling solution of potash; dissolves in hydrochloric acid with evolution of chlorine, forming a brown liquid, which is turned green by alcohol; dissolves also in dilute sulphuric or nitric acid, forming an orange-yellow solution. (Warington, *Phil. Mag. J.* 21, 380.) Sparingly soluble in water. (Grouvelle; see also Reinsch, *Pogg.* 55, 97.)

	Dried at 100°		Warington.	Reinsch.
2MnO	72	50·71	51·07	50·9
CrO^3	52	36·62	36·71	37·3
2HO	18	12·67	12·20	11·8
$MnO, CrO^3 + 2Aq$	142	180·00	99·98	100·0

b. Monochromate?—Aqueous chromic acid slowly dissolves manganese with evolution of hydrogen gas; manganous oxide and its carbonate, however, are more readily dissolved by it. Uncrystallizable, chestnut-brown liquid, having an acid reaction and pungent metallic taste. After repeated evaporation, it deposits nearly all the manganese in a higher state of oxidation. (John.)—Neither the monochromate nor the bichromate of potash precipitates manganous salts immediately; after some time, however, especially with the monochromate, a brownish black precipitate is produced. (Thomson.)

OTHER COMPOUNDS OF MANGANESE.

With Iron, Cobalt, Nickel, Copper, and Gold, forming white, brittle, and very refractory alloys.

CHAPTER XXIV.

ARSENIC.

Scheele. *Opusc.* 2, 28; also *Crell. N. Entd.* 3, 125.
Bergman. *Opusc.* 2, 272.
Bucholz. Arsenic Acid. *Scher. J.* 9, 397.—Arsenious Acid. *Schw.* 15, 337.
Laugier. *Ann. Chim.* 85, 26.
Fischer. *Schw.* 6, 236; 12, 155; 39, 364.—*Kastn. Arch.* 11, 224.
Thomson. Degrees of Oxidation of Arsenic. *Ann. Phil.* 4, 171; also *Schw.* 17, 422.—Salts of Arsenic Acid. *Ann. Phil.* 15, 81; also *Schw.* 29, 430.

Berzelius. *Ann. Chim. Phys.* 5, 179; 11, 225.
Gehlen. Behaviour of Arsenic with Potash. *Schw.* 15, 501.
Gay-Lussac. Behaviour of Arsenic with Potash. *Ann. Chim. Phys.* 3, 136.
Pfaff. Arsenic Acid. *Schw.* 45, 5·9.
Buchner. Arsenic Acid. *Schw.* 45, 419.
Guibourt. *J. Chim. med.* 2, 55.
Stromeyer. De hydrogenio arsienato. *Comment. Soc. Gott.* 16, 141.
Proust. Arseniuretted Hydrogen. *Scher. J.* 8, 285.—Sulphide of Arsenic. *Scher. J.* 9, 287; also *Gilb.* 25, 178.
Thénard. Sulphide of Arsenic. *Ann. Chim.* 59, 284; also *N. Gehl.* 2, 685.
Berzelius. Sulphide of Arsenic and its combinations with other Metallic Sulphides. *Schw.* 34, 46. Further: *Pogg.* 7, 1 and 137.
Dumas. Arseniuretted Hydrogen and Chloride of Arsenic. *Ann. Chim. Phys.* 33, 351; also *Pogg.* 9, 308.
Dumas. Solid Arsenide of Hydrogen and Arseniuretted Hydrogen gas. *J. Pharm.* 16, 335; also, *Pogg.* 19, 191; abstr. *Schw.* 59, 222.
Graham. Arseniates. *Phil. Trans.* 1833, 2, 253; also *Pogg.* 32, 33.
Bouquet & Cloez. New Acid containing Sulphur, Arsenic, and Oxygen. *N. Ann. Chim. Phys.* 13, 44; *J. Pharm.* 7, 23; abstr. *Ann. Pharm.* 56, 205.
Walchner. Distribution of Arsenic and Copper. *Compt. rend.* 23, 12; also *Ann. Pharm.* 61, 205.
Bussy. Modifications of Arsenious Acid. *Compt. rend.* 24, 774; *Phil. Mag. J.* 31, 151; *Repert. Pharm.* 2nd ser., 48, 301; *Ann. Pharm.* 64, 286; *J. pr. Chem.* 41, 340; *Pharm. Centr.* 1847, 938; *J. Pharm. Chim.* 12, 321.
Will. Occurrence of Arsenious Acid and other Metallic Oxides in Mineral Waters. *Ann. Pharm.* 61, 192.
Pasteur. Chloride of Arsenic. *J. Pharm. Chim.* 13, 395; abstr. *Ann. Pharm.* 68, 307. Salts of Arsenious Acid. *J. Pharm. Chim.* 13, 397; abstr. *Ann. Pharm.* 68, 308.
Filhol. Salts of Arsenious Acid. *J. Pharm. Chim.* 14, 331 and 401; abstr. *Ann. Pharm.* 68, 308.

Arsen, Arsenik, Scherbenkobold, Näpchenkobold (*Goblet-fiend, Bowl-sprite*), *Fly-poison, Cobaltum* of the druggists.

History. Known from very early times, principally in the forms of sulphide of arsenic and arsenious acid. Brandt, in 1733, made the first accurate experiments on its chemical nature. Scheele, in 1755, discovered arsenic acid and arseniuretted hydrogen gas. Sir H. Davy discovered the solid arsenide of hydrogen. Berzelius specially investigated the stoïchimetrical relations of arsenic and its numerous sulphur-compounds.

Sources. Native; as arsenic acid; as arseniate of lime, magnesia, lead-oxide, ferrous, ferroso-ferric, and ferric oxide, cobaltic oxide, nickel-oxide, and cupric oxide; as sulphide of arsenic combined with other metallic sulphides, as in Grey copper, Tennantite, Light red silver, and Argentiferous copper-glance; in combination with another metal, in arsenide of manganese, arsenide of iron, arsenide of cobalt, and arsenide of nickel; in combination with another metal and a metallic sulphide, in Arsenical pyrites, Cobalt-glance, Nickel-glance, and many varieties of Antimonial nickel. Small quantities of arsenic and its compounds are likewise found in other minerals and products obtained from them, as in sulphur, sulphuric acid, phosphorus, phosphoric acid, sulphide of antimony and preparations made from it, and in zinc, tin, and many varieties of ferric oxide. Traces of arsenic are likewise found in the Olivine which accompanies the Siberian meteoric iron (of Pallas) and that from Atacama (not in terrestrial olivine). (Rumler, *Pogg.* 49, 591.) ¶ Walchner has shown that arsenic (together with copper) is as widely distributed as iron, small quantities of these metals being invariably found in iron-ores, whether occurring in ancient or modern formations, in all chalybeate waters and the deposits formed from them, and in a great variety of ferruginous clays, marls, and slates. Walchner has likewise demonstrated the presence of minute quantities of arsenic and copper in various specimens of meteoric iron, viz. in the Siberian meteoric iron above mentioned (Rummler had merely shewn the existence of arsenic in the accompanying olivine), in a Mexican sample from Yuanhuitlan, near Oaxaca; in a specimen from Tenessee, and in the large mass preserved in the Cabinet of Natural History of the Yale College, Connecticut. Hence it would appear that arsenic and copper are associated with iron in the other bodies of the universe as well as on the earth. (*Ann. Pharm.* 61, 209.) The presence of arsenic in mineral waters has likewise been demonstrated by Will (*Ann. Pharm.* 61, 192.)¶ The statement of Orfila & Couerbe (*J. Chim. med.* 15, 462 and 632) that arsenic is contained in the bones and muscular flesh of a healthy man, and in the bones of a healthy horse, ox, and sheep, was attacked by Danger & Flandin and by Chevallier (*J. Chim. med.* 17, 84), by Barbet, Fauré & Magouty (*J. Chim. med.* 17, 654), by Pfaff (*Repert.* 74, 106), by Steinberg (*J. pr. Chem.* 25, 384), and by Jacquelain (*Compt. rend.* 16, 30), and has since been retracted by Orfila himself (*Ann. Chim. Phys.* 77, 159) as unfounded.

Preparation on the large scale.—By heating arsenical pyrites in earthen tubes till the arsenic sublimes.—Under these circumstances, the arsenical pyrites Fe^2,As,S^2, is resolved into $2FeS$ which remains behind and As which sublimes. The tubes, several of which are laid together horizontally in the furnace, are 3 feet long and 1 foot wide. A tube, 8 inches long, made by rolling up a piece of iron plate, is inserted for half its length into the part of the earthen tube which projects from the furnace, and an earthen receiver is luted on to it. The arsenic sublimes in the iron tube in the form of a coherent, internally crystalline mass, which, when the whole has cooled, is detached by unrolling the tube.

Purification.—By a second sublimation.—Commercial arsenic is contaminated, partly with suboxide and sulphide of arsenic, which are more volatile than the metal itself, partly with fixed impurities, such as earthy matrix, undecomposed arsenical pyrites, &c. On subliming this impure arsenic, the suboxide and sulphide volatilize first, and either condense in the cooler part of the apparatus or escape in the form of vapour, while the arsenic itself condenses nearer to the fire. The addition of charcoal powder is useful. The apparatus consists either of two crucibles placed one above the other and luted together with clay, the under one, which contains the crude arsenic, being thrust half-way through a hole in an iron plate, so that the fire may act only on its lower part; or of a glass flask half-filled with crude arsenic, and having a glass tube fastened to its neck with loam, which is afterwards dried: the tube is loosely closed at top with a charcoal stopper. The flask is immersed to two-thirds of its depth in a crucible filled with sand, and the crucible surrounded with red-hot coals. The arsenic condenses on the upper part of the flask; but, as the air cannot be completely excluded, it is always more or less contaminated with octohedrons of arsenious acid. (*Comp.* Bette, *Ann. Pharm.* 33, 355.) To obtain the arsenic quite free from suboxide and arsenious acid, it must be sublimed in a wide tube in a stream of dry hydrogen gas. Small quantities only must be operated upon at once, otherwise the tube will be stopped up by the sublimed arsenic. On the small scale, also, metallic arsenic may be obtained by igniting a mixture of arsenious acid and black flux (III., 20) in a subliming apparatus of this description, or by igniting arseniate of lime in a retort through which hydrogen gas is passed.

Properties.—Crystalline system, the rhombohedral. Form, an acute rhombohedron. *Fig.* 151; $r^3 : r^5 = 85° 26'$. Cleavage parallel to r and p. A more acute rhombohedron likewise occurs, as also an obtuse rhombohedron, *Fig.* 141 in which $r^3 : r^5 = 114° 26'$, and one still more obtuse. (Breithaupt, *Pogg.* 7, 527; *Schw.* 52, 168.) According to former statements, and likewise according to that of Elsmer (*J. pr. Chem.* 22, 344), arsenic appears to crystallize in octohedrons; perhaps, however, the truncated acute rhombohedron (*Fig.* 153) was mistaken for that form. Specific gravity = 5·621, Karsten; 5·672, Herapath; 5·76, Lavoisier; 5·959, Guibourt, (8·31, Bergman.) Not very hard, but very brittle. Tin-white, inclining to steel-grey; very bright. Volatilizes at a dull red heat, without previously fusing. In a glass tube it does not volatilize even at 294° (561° F.); not even at the melting point of zinc, but begins to volatilize at a red heat visible in the dark. (Mitchell.) If an attempt be made to fuse it by heating it in a sealed glass tube, the tube bursts, but no fusion takes place. (Fischer.) Arsenic is a violent poison.

¶ According to Berzelius (*Ann. Pharm.* 49, 247), arsenic exists in two allotropic states. One of these, As α, is produced when arsenic, in the state of vapour and mixed with another heated gas, is deposited on a part of the subliming apparatus which is not very strongly heated. It is dark grey, crystalline, and oxidizes in the air, especially at 40°, being thereby converted into black pulverulent suboxide. The other modification, As β, is produced when arsenic is very strongly heated, or when it condenses by sublimation on a part of the vessel the temperature of which is near the point at which the arsenic volatilizes, so that the metal is deposited in an atmosphere of its own vapour. This modification is nearly white, has a strong metallic lustre, is denser than the preceding, and remains unaltered in the air, even though finely pounded and heated to 70° or 80°, and perhaps even above 100°. These modifications of the metal appear to be repeated in arsenious acid, which likewise exhibits two varieties of structure, the crystalline and the vitreous (*vid. pp.* 254, 255). The former of these, which is produced when the acid condenses on a cold surface, or when it crystallizes from a hot aqueous solution, appears to have As a for its radical; while the latter, which is formed when the acid sublimes on a strongly heated surface, is probably derived from As β. [May not these so-called allotropic modifications be attributed to difference of mechanical structure? The circumstances under which the modification As β is produced admit of slower cooling, and consequently allow the particles to arrange themselves with greater regularity and compactness:

hence greater density and greater power of resisting the action of oxidizing agents, &c. Many other cases of *allotropic* modification may be explained in a similar manner. (W.)] ¶

Compounds of Arsenic.

ARSENIC AND OXYGEN.

A. SUBOXIDE OF ARSENIC.

Most metallic arsenic when exposed to moist air at ordinary temperatures, gradually becomes covered with a black film, and finally crumbles to a black powder. Many specimens of metallic arsenic (the denser variety most probably) retain their lustre and solidity when exposed to the air, and do not increase in weight. (Berzelius, Buchner, *Repert.* 21, 28; Thomson, *Ann. Phil.* 18, 130.) In dry air, arsenic remains unaltered; and after long exposure to dry air, it remains unchanged for a longer time in moist air, probably in consequence of the deposition of foreign matter (films of organic matter) on its surface. But when exposed in the fresh state to moist air, its surface soon assumes a bronze colour, and in a few days becomes covered with suboxide; between 30° and 40°, this change takes place more quickly. Lumps of the metal, however, never fall to pieces, but merely acquire a coating of suboxide. If water condenses on the pulverized arsenic, arsenious acid is immediately produced. (Bonsdorff.)

Properties.—Brownish black; more volatile than arsenic, less volatile than arsenious acid; in the state of vapour it has an odour of garlic, or like that of phosphorus. When arsenic is heated in a tube containing air, by immersion in zinc just solidified after fusion, a white ring of arsenious acid sublimes, and below it a brown ring of suboxide; and if the tube be then immersed in boiling mercury, the white ring volatilizes, but the brown ring remains until it is converted by oxidation into arsenious acid, whereupon it likewise passes off in vapour. (Mitchell.)

Approximate calculation.

As	75	....	90·36
O	8	....	9·64
AsO	83	....	100·00

The calculation is based upon the fact, that 100 parts of pulverized arsenic exposed to the air, take up at most 8 parts of oxygen, according to Berzelius, and 11 parts according to Bonsdorff.

Proust regards the suboxide as a mere mixture of metallic arsenic and arsenious acid: if that were the case, however, the oxidation ought to go on till the whole was converted into arsenious acid.

Decompositions.—When gently heated out of contact of air, the suboxide is resolved into arsenious acid which volatilizes, and metallic arsenic which remains behind. (Berzelius, Mitchell.) When it is digested in hot hydrochloric acid, arsenious acid is dissolved, and metal remains behind. (Berzelius.) Insoluble in water and in cold acids.

B. Arsenious Acid. AsO^3.

Oxide of Arsenic, White Arsenic, Flowers of Arsenic, Rat-poison, Hüttenrauch, Giftmehl, Arsenige Säure, Acide arsenieux, Arsenoxyd, Oxyde d'Arsenic.

Formation.—Arsenic, heated in the air till it volatilizes, burns with a reddish smoke having the odour of garlic, and is converted into arsenious acid; when more strongly heated, it burns with a pale blue flame. A piece of arsenic held for a moment by the tongs in the flame of a candle, burns for a while with a pale blue flame; and when this ceases, the metal continues to waste away, producing a brownish smoke, until it is almost entirely consumed. Even arsenic which has been purified by sublimation in hydrogen gas, continues to burn away slowly when set on fire. The arsenious acid appears to be at first accompanied by suboxide of arsenic, which produces the reddish or brownish white, garlic-smelling fume, and to be afterwards wholly converted into arsenious acid: for the vapour of pure arsenious acid does not emit the garlic odour, and metallic arsenic does not volatilize at the comparatively low temperature at which the combustion goes on. Hence, if burning arsenic be thrown into a glass tube, no sublimate of metal is formed. (Mitchell, *Sil. Am. J.* 19, 122.) ¶ Schönbein suggests that the garlic-odour emitted by arsenic may be due, not to the formation of a suboxide, but to a peculiar modification of arsenious acid, As^2O^6, which is subsequently converted into ordinary arsenious acid, $2AsO^3$. (*Pogg.* 75, 377.) ¶—2. Arsenic, when covered with water, and exposed to the air at ordinary temperatures, is converted into arsenious acid. The water absorbs the oxygen of the air, transfers it to the arsenic, and dissolves the arsenious acid as it forms. If air be blown into water through which pounded arsenic is diffused, the liquid, after ten or fifteen minutes, gives a strong yellow colour with hydrosulphuric acid. (Orfila, *J. Chim. Med.* 6, 6.) If the arsenic powder is merely moistened with water, it oxidates still more quickly. This circumstance may perhaps explain the observation of Boullay (*J. Pharm.* 13, 433), and of Schwabe (*Br. Arch.* 11, 262), namely, that pounded arsenic in large quantities, (8 lbs. for example) becomes heated by exposure to the air. In the instance mentioned by Boullay, the heat was so great as to set fire to the arsenic; and when the combustion was stopped by moistening with water, it broke out again, after several days, in a quantity of the arsenic which had been sent away in a packet. According to Büchner (*Br. Arch.* 19, 258), this rise of temperature takes place only when the arsenic is moistened with water during pulverization.—3. Arsenic vapour passed, together with vapour of water, through a red-hot tube, yields but very little hydrogen gas. (Regnault, *Ann. Chim. Phys.* 62, 364.)—Pure water boiled with arsenic, dissolves a small quantity of arsenious acid, while solid arsenide of hydrogen is left behind, in the form of a brown powder. (Orfila.)—Arsenic heated, but not to redness, with hydrate of potash, forms arsenite of potash and arsenide of potassium, and liberates hydrogen gas. (Soubeiran.) [For further development of this matter, vid. *Formation of Arsenic* acid, 6, p. 260.] At ordinary temperatures, and out of contact of air, arsenic undergoes no alteration when immersed in water freed from air by boiling. (Bonsdorff.)—4. With boiling oil of vitriol, arsenic forms arsenious acid and liberates sulphurous acid; with dilute nitric acid, it likewise forms arsenious acid and liberates nitric oxide. Strong hydrochloric acid boiled with arsenic, neither dissolves the metal nor gives off hydrogen. (H. Rose, Gmelin.) Berthollet maintains the contrary. (*Stat. chimique*, *2, 395.*)

Preparation.—By roasting arseniferous minerals in a furnace, from which the fumes are conveyed into a horizontal condensing chamber, called the *Poison-trap* (*Giftfang*), or into a building called the *Poison-tower* (*Giftthurm*), containing a number of chambers, placed one above the other. The *Poison-meal*, or *Arsenic-meal*, (*Giftmehl*, *Arsenikmehl*,) which condenses in these chambers, is introduced either alone, or mixed with a small quantity of crude potash to retain the sulphur, into an iron pot, on which a number of cylindrical iron rings are luted one above the other, and heated till it volatilizes. The greater part of the arsenious acid condenses on the rings at a temperature near its melting point, and sinters together into a vitreous mass, called *white arsenic-glass*. The uncondensed portion of the vapour is carried from the uppermost ring through a tube into a condensing chamber, in which it solidifies in the form of *meal*.—The product is purified from any sulphide of arsenic accidentally present, by mixing it with a small quantity of potash, and subliming it again. Arsenic-glass, *e. g.*, that from Andreasberg, frequently contains oxide of antimony, a portion only of which can be separated by sublimation. By digestion in cold hydrochloric acid, the antimonic oxide is gradually dissolved in preference to the arsenious acid; hence the resulting solution, when treated with hydrosulphuric acid, gives first a yellowish red and then a yellow precipitate. On dissolving the precipitate in hot nitric acid, a residue is left, consisting of antimonic oxide mixed with arsenic acid; this residue dissolves readily in hydrochloric or tartaric acid, yielding a solution which gives all the reactions of antimonic oxide. (Wiggers, *Ann. Pharm.* 41, 347.)

Properties.—Arsenious acid occurs in two crystalline forms, and likewise in the amorphous state.

a. Octohedral Arsenious Acid.—Obtained: 1. In the sublimation process, when the vapour is so quickly cooled that the acid solidifies at once, without passing through the semifused state. *Arsenic-meal* likewise belongs to this variety, but it is generally contaminated with metallic arsenic, sulphide of arsenic, and other impurities.—2. By the cooling of a hot saturated aqueous solution.—3. When white arsenic-glass is preserved for a long time, under which circumstances it becomes opaque and acquires a texture like that of porcelain or enamel.—*Opaque Arsenic-glass*, when obtained as in (1) or (2), forms regular octohedrons and tetrahedrons, which are transparent and have a strong lustre. Specific gravity of the opaque arsenic-glass, 3·529 (Taylor, *Phil. Mag. J.* 9, 482), 3·695 (Guibourt); that of arsenious acid obtained by digesting arsenic in nitric acid and washing with water, is 3·7202 (Karsten).

b. Right-rhombic Arsenious Acid.—This variety is, in a very few instances, obtained by sublimation, and appears to be isomorphous with native oxide of antimony. In a furnace in which cobalt-ore was roasted, arsenious acid was found sublimed in transparent, colourless, thin, flexible, six-sided tables, having a pearly lustre, and a plane of cleavage parallel to the principal face (with octohedrons attached to them here and there). These crystals, when sublimed or dissolved in hot water, and left to separate by cooling, were converted into octohedrons and tetrahedrons; they were free from arsenic acid. (Wöhler, *Pogg.* 26, 177.)—¶ If a boiling solution of potash be saturated with arsenious acid and left to cool, the arsenious acid gradually separates from it, and almost always in right rhombic crystals, isomorphous with native oxide of antimony. (Pasteur, *Compt. rend.* 24, 774.) ¶

c. Amorphous Arsenious Acid.—Newly prepared, transparent arsenic-glass is in this state. Specific gravity=3·698, at 4° in vacuo (Le Royer & Dumas); 3·7026 (Karsten); 3·7385 (Guibourt); 3·798 (Taylor). Transparent and colourless glass, with conchoïdal fracture. The transparent vitreous acid becomes turbid in a few months at ordinary temperatures, and afterwards white and opaque; according to Fuchs (*Schw.* 67, 429), this change takes place in proportion as the acid passes from the amorphous to the crystalline state. Vitreous arsenious acid becomes opaque, both in the open air and in close vessels containing air. At 100°, according to Regnault (*Ann. Chim. Phys.* 76, 144), the opacity comes on quickly. On the other hand, the glass remains transparent for years when kept under water (Christison, *Pogg.* 36, 494), or under alcohol, or alone in a vessel from which air is completely excluded (H. Rose, *Pogg.* 52, 454). Under hydrochloric acid, on the contrary, it becomes opaque. (Wiggers.) According to Krüger (*Kastn. Arch.* 2, 473), the glass becomes opaque only when in contact with moist air, and the change is accompanied by an increase in weight, amounting to $\frac{1}{160}$. When from 1 to 1½ parts of transparent arsenious acid are dissolved by half an hour's boiling, in a mixture of 6 parts of fuming hydrochloric acid and 2 parts of water, and the solution left to cool as slowly as possible, the arsenious acid crystallizes in transparent octohedrons, and the formation of each crystal is accompanied by a spark; on agitation, which gives rise to the formation of many new crystals, a corresponding number of sparks is produced. If from 4 to 6 parts of arsenic-glass are dissolved in the above-mentioned mixture, the light produced by the crystallization is sufficient to illuminate a dark room. As long as the deposition of crystals goes on, so long is light perceived on agitating the liquid; and this appearance may be visible on the second, and even, though very faintly, on the third evening. If the liquid be then boiled, so as to dissolve the remaining portion of the vitreous acid, crystallization again takes place, accompanied by emission of light, though not so bright as before. If the liquid be rapidly cooled, the acid separates in the pulverulent state, and little or no light is emitted. A solution of arsenious acid in a hot mixture of hydrochloric and nitric acid, the quantity of the latter not being sufficient to convert the whole of the arsenious acid into arsenic acid, likewise emits a strong light as the acid crystallizes. Boiling dilute sulphuric acid dissolves arsenious acid in smaller quantity, and exhibits only occasional luminosity. Nitric and acetic acid, which dissolve still less of the arsenious acid, exhibit no luminosity whatever. Arsenious acid, which has acquired the porcelain texture, and likewise arsenic meal, exhibit, when dissolved in hydrochloric acid, a very feeble luminosity on agitation. (H. Rose, *Pogg.* 35, 48.)

Arsenious acid, when heated suddenly or under increased pressure, melts to a glass. The vitreous arsenious acid *c* may be fused before it volatilizes to any considerable extent; the crystallized acid *a* appears to have a higher melting point, and evaporates before fusion. (Wöhler, *Ann. Pharm.* 41, 155.) The acid does not volatilize at ordinary temperatures. (Faraday, *Pogg.* 19, 501.) It volatilizes more readily than the metal, at 218°, according to Mitchell. Specific gravity of the vapour=13·85. (Mitscherlich.) The colourless vapour emits no smell of garlic. (Scheffer, Fischer.) It is only when the acid is heated on deoxidizing substances, such as charcoal or iron, that the garlic odour becomes perceptible.—Arsenious acid in solution reddens litmus slightly. According to Guibourt, it is only the solution of the transparent acid prepared hot and then cooled that reddens litmus; whereas, according to the same authority, the solution of that which has become opaque turns reddened litmus blue; Gmelin, however, found that the solution of the latter likewise reddened litmus slightly. The acid has a rough taste, slightly metallic, and afterwards sweetish. It is one of the most violent among the acrid poisons.

			Thomson.	Thénard.	H. Davy.	Proust.
As	75	75·76	70·37	74·24	75	75·2
3O	24	24·24	29·63	25·76	25	24·8
AsO^3	99	100·00	100·00	100·00	100	100·0

	Mitscherlich.	Berzelius.	Richter.
As	75·73	75·782	86·86
3O	24·27	24·218	13·14
	100·00	100·000	100·00

	Vol.	Sp. gr.
Arsenic vapour	1	10·3995
Oxygen gas	3	3·3279
Arsenious acid vapour	1	13·7274

(As^2O^3 = 2 . 470·04 + 3 . 100 = 1240·08. Berzelius.)

Decompositions.—An aqueous solution of arsenious acid placed in the voltaic circuit, yields oxygen at the positive pole, arseniuretted hydrogen gas and metallic arsenic at the negative pole; less quickly however than arsenic acid. (Bischof; *comp.* Simon, I., 393.)—2. At a heat short of redness, hydrogen, carbon, carbonic oxide, phosphorus, sulphur, potassium, sodium, and zinc (the last three with vivid combustion: *Gay-Lussac & Thénard, Gehlen*), and other metals, withdraw all the oxygen from arsenious acid, forming respectively, water, carbonic acid, phosphoric acid, sulphurous acid, or a metallic oxide; arsenic reduced by phosphorus or sulphur enters into combination with a portion of these substances. If a small quantity of arsenious acid be placed at the bottom of a narrow glass tube,—a slip of charcoal just over it—and the heat of a spirit-lamp applied, first to the charcoal and then to the arsenious acid, metallic arsenic sublimes on the cold part of the tube. If a mixture of arsenious acid and carbonate of soda be placed upon charcoal and exposed to the inner blowpipe flame, the garlic odour becomes perceptible. (Berzelius.)—3. Aqueous phosphorous or hypophosphorous acid, boiled down with arsenious acid till phosphuretted hydrogen begins to escape, reduces the arsenic.—4. From the aqueous solution, zinc, cadmium, and tin precipitate the arsenic very slowly; on the addition of hydrochloric acid, these same metals reduce the arsenic more quickly; and under the same circumstances, the reduction is likewise effected, though more slowly, by antimony, bismuth, lead, and copper. The reduction is never complete; zinc throws down brown pulverulent arsenide of hydrogen; iron does not reduce the arsenic, but becomes oxidated and forms arsenite of ferric oxide. (Fischer, *Pogg.* 9, 260.) When hydrochloric acid is present, however, the greater part of the arsenic escapes in the form of arseniuretted hydrogen gas.—5. Arsenious acid heated with lime is resolved, according to Wollaston, without evolution of light or heat, into arseniate of lime, and sublimed metallic arsenic; according to Gay-Lussac, a similar reaction takes place with carbonate of potash. In the former case, arsenite of lime is formed as well as arseniate, the quantity being greater as the ignition is less intense. (Simon.)—6. Arsenious acid dissolved in water and mixed with a stronger acid, is quickly decomposed by sulphuretted hydrogen, yielding tersulphide of arsenic and water: $AsO^3 + 3HS = AsS^3 + 3HO$.

Combinations.—a. With Water.—*Aqueous Arsenious Acid.*—Arsenious acid dissolves very slowly in cold water, but more quickly in boiling water. A hot saturated solution contains 1 part of arsenious acid in 10 or 12 parts of water; on cooling, part of the acid separates in small anhydrous crystals, leaving a solution containing 1 part of the acid in 20 or 30 parts of water.

One part of arsenious acid dissolves in 7·72 parts of boiling water, if it has previously become opaque, and in 9·33 parts if it is still transparent (Guibourt); in 10·5 (Wenzel); in 11·34 (Fischer); in 12 (Klaproth); in 12·2 (Bucholz); in 15 (Brandt, Justi, Bergman); in 16 (Rud. Aug. Vogel); in 21 if the acid is transparent, and in 24, if it is opaque (Taylor); in 24 (Lametherie); in 40 (Pörner); in 64 (Baumé); in 80 (Navier); in 200 (Nasse); in 640 (Hagen).—To dissolve 1 part of arsenious acid in 12 parts of water, it is necessary to boil an excess of it with the water; if 1 part of the acid is boiled with only 12 parts of water, a considerable quantity remains undissolved; even with 1 part of the acid in 50 or 60 parts of water, long continued boiling is necessary to effect complete solution.—If a solution saturated by long boiling with excess of acid and then poured off from the undissolved portion, be boiled down continuously to one-half of its bulk, the whole of the acid remains dissolved, so that the concentrated liquid contains 1 part of acid in 6 parts of water. (Fischer.)

After this solution has been left to stand for some time at ordinary temperatures, 1 part of arsenious acid remains dissolved in 16 parts of water at 16°, and in 20 parts at 7° (Bucholz); in 33 (Klaproth); in 38·45 after 3 days, and 55 after 8 days, and in 64·5 after 2 or 3 weeks at 10° (Fischer); in 33·52, if the acid had become opaque before it was dissolved, and in 55·06 if it was transparent at the time of solution (Guibourt); in 38 water after half a year, if it was opaque, and in 53....71 water after 48 hours, if it was transparent. (Taylor.)

When pulverized arsenious acid in excess is left to digest for several days in cold water, 1 part of it dissolves in 50 parts of the water (Bucholz); in 66 (Fischer); in 80 (Bergman); in 80, if it had become opaque, in 103 if it was still transparent (Guibourt); in 96 at 10° (Spelman); in 96 at 35° (Kahnemann); in 320 at 20° (Nasse, *Schw.* 5, 217); in 400 (Klaproth, *Schw.* 6, 231).

If one part of pulverized arsenious acid be digested for 10 days at 19°....25°, in 5....10 parts of water, the resulting solution contains 1 part of acid in 50 parts of water; a solution of the same strength is obtained in 25 days by digesting 1 part of the acid in 40 parts of water. If 1 part of the acid be immersed in 80 parts of water, the resulting solution contains $\frac{1}{90}$; with 160 parts of water, $\frac{1}{180}$; with 240 water, $\frac{1}{280}$; with 1000 water, $\frac{1}{1200}$: and even when 1 part of acid is digested at ordinary temperatures for several days with 16,000....100,000 parts of water, a portion still remains undissolved.—Pulverized opaque arsenious acid was immersed in various proportions of water, and the liquid set aside in closed bottles and in a cool place. After 18 years, the following results were obtained: 1 part of arsenious acid in 1000 parts of water: perfect solution; the liquid contained nothing but arsenious acid and arsenic acid.—1 part of arsenious acid in 100 parts of water: 0·017 pt. acid remained undissolved.—1 part of acid in 35 parts of water: the undissolved portion amounted to 0·35 pt., so that the solution contained 1 part of acid in 54 of water. (Gm.)

The cause of this very slow solution of arsenious acid in cold water is to be found in the small adhesion and affinity of water for arsenious acid and the great cohesive force of the latter. Fischer's supposition—that arsenic-glass only dissolves in water in so far as it takes up more oxygen, and that when cold water is used, the oxidation takes place by unequal distribution of the oxygen, so that a grey oxide of arsenic containing less oxygen remains undissolved, whereas when the acid is digested in hot water, it is oxidated by the oxygen of the water, but in such a manner that the hydrogen is not set free in the gaseous form, but remains in the liquid in a state of loose combination—is directly contradicted by experiment: for Bucholz and Pfaff, as well as Gmelin, found that pure arsenic-glass is perfectly soluble in cold water; and as to oxidation by the oxygen of the water, in such a manner that the hydrogen is not set free but remains in the liquid without entering into any other state of combination—we can only say that it is a process of which no definite idea can be formed. (See also Phillips, *Ann. Phil.* 8, 152.)

¶ Bussy finds that the vitreous acid dissolves more quickly and more abundantly in water than that which has become opaque; the same quantity of water which at 12° or 13° will take up 36 or 38 parts of the former, will not dissolve more than 12 or 14 of the latter. By long boiling with water, the opaque acid is converted into the transparent variety—that is to say, it acquires the solubility of the latter, so that a litre of the fluid takes up 110 grammes of the acid. On the other hand, by the continued action of water and of a low temperature, the vitreous acid is converted into the opaque—that is to say, the solution, after a while, becomes weaker, retaining only the proportion of acid which corresponds to the solubility of the opaque variety. Comminution diminishes the solubility of the opaque and increases that of the vitreous acid. Arsenious acid which has been rendered opaque by the action of ammonia, and that which has been crystallized from an aqueous solution, are equally soluble in water. The anomalies relating to the solubility of arsenious acid in water may perhaps be due to the simultaneous occurrence of both modifications of it in the solution.—The solutions of the two varieties affect litmus in the same manner.—The opaque acid dissolves more slowly in hydrochloric acid than the vitreous modification. (*Compt. rend.* 24, 774; Liebig & Kopp's *Jahresbericht*, 1847—1848, 422.) ¶

The solution of arsenious acid in water is transparent and colourless, and reddens litmus slightly. Sulphuretted hydrogen water colours it yellow, and, on the addition of a stronger acid, throws down a yellow precipitate. It gives a white precipitate with excess of lime-water; siskin-green (*Scheele's green*) with an ammonia-salt of copper (ammonio-nitrate or sulphate, for example); and on the addition of a small quantity of alkali, a white precipitate with nitrate of mercurous oxide and corrosive sublimate, and an egg-yellow precipitate with nitrate of silver. It colours the red solution of permanganate of potash brown-yellow (after standing for a few days, the mixture becomes decolorized and deposits brown flakes); turns the yellow colour of chromate of potash to green (vid. *Arsenic and Chromium*, p. 312); decolorizes the aqueous solution of iodine or bromine; produces, when mixed with hydrochloric acid, a grey metallic deposit on copper; and evolves arseniuretted hydrogen gas with zinc and hydrochloric acid.

The limit of the yellow colouring by hydrosulphuric acid is attained with 1 part of arsenious acid in 10,000 parts of water. (Lassaigne, *J. Chim. med.* 8, 584).—That of the yellow precipitation by hydrosulphuric acid in presence of hydrochloric acid, with 1 part of arsenious acid in 80,000 of liquid (Lassaigne); 1 pt. in 90,000 (Reinsch, *J. pr. Chem.* 13, 133); 1 pt. in 160,000 (Brandes & Ebeling, *Br. Arch.* 25, 269.)—Lime-water does not precipitate a solution of arsenious acid containing less than 1 part of acid in 4000 parts of water (Harting, *J. pr. Chem.* 22, 49); according to Lassaigne, the limit is 1 part of acid in 5000 of water.—The limit of the precipitation by ammonio-sulphate of copper is 1 part of arsenious acid in 160,500 of water (Lassaigne); 1 in 250,000 (Brandes & Ebeling); the precipitate, however, does not show its characteristic colour if the proportion of acid is less than 1 in 12,000. (Harting.)—The green colouring of chromate of potash will indicate the presence of 1 part of arsenious acid in 1000 parts of water. (Brandes & Ebeling.)—The aqueous solution of arsenious acid mixed with hydrochloric acid quickly produces a grey metallic deposit on a clean plate of copper. (By a solution of arsenious acid in strong hydrochloric acid, this deposit is not produced till after the lapse of several days or even weeks at ordinary temperatures, but immediately on the application of heat.) On boiling the liquid, the deposit turns black and peels off in black scales. The grey deposit is immediately produced on boiling, even in a solution containing only 1 part of arsenious acid in 100,000 parts of water; in a solution containing 1 part in 200,000 the deposit takes half an hour to form; and the limit of the reaction is about 1 part in 250,000....300,000. Aqueous arsenious acid without hydrochloric acid has no action on copper. (Reinsch, *J. pr. Chem.* 21, 244.)

b. With the stronger acids, arsenious acid forms salts in which it plays the part of a base, and which may therefore be called SALTS OF ARSENIC OXIDE. In some acids, especially in certain mineral acids, arsenious acid is scarcely soluble excepting on the application of heat, and separates again almost completely on cooling; hydrochloric acid and certain vegetable acids retain a considerable quantity of it even in the cold. The salts of arsenic oxide are precipitated yellow by hydrosulphuric acid, yield arseniuretted hydrogen and metallic arsenic when treated with zinc, and deposit metallic arsenic on polished copper.

c. With Salifiable Bases, arsenious acid forms salts called ARSENITES. The affinity between the acid and base in these salts is very slight; hence they are decomposed by many other acids, even by carbonic acid, and deposit a white powder. Most arsenites, when heated alone, are decomposed; some of them allow the acid to volatilize, while the base remains; the arsenites of the fixed alkalis, and a few others, give off arsenic and leave a salt of arsenic acid ($5AsO^3 = 3AsO^5 + 2As$). Arsenite of silver gives off arsenious acid, and leaves a mixture of arseniate of silver and metallic silver; arsenite of lead alone withstands a red heat without decomposition, and arsenite of magnesia is but very imperfectly decomposed. (Simon, *Pogg.* 40, 435.) When heated with charcoal powder, the arsenites give off metallic arsenic; under such circumstances, however, —*e. g.*, in the case of copper—a metallic arsenide may be formed. A mixture of an arsenite with charcoal powder (especially on the addition of borax) or with oxalate of lime, ignited in a bulb blown at the end of a narrow glass tube, yields a sublimate of metallic arsenic. Arsenites ignited with carbonate of soda upon charcoal, in the inner blowpipe flame, emit the odour of garlic. Those arsenites, which are insoluble in water, dissolve in hydrochloric acid, and several of them also in sulphate, hydrochlorate, and nitrate of ammonia. Alkaline arsenites, dissolved in water, give white precipitates with lime-water and lime-salts; yellowish green with cupric salts; egg-yellow with nitrate of silver. Hydrosulphuric acid gives no precipitate unless a stronger acid is likewise present; but all arsenites which are not soluble in water, are, when dissolved in hydrochloric acid, immediately precipitated by hydrosulphuric acid; and if the metallic oxide with which the arsenious acid is combined, is likewise precipitable by hydrosulphuric acid, a compound metallic sulphide may be produced.

d. Arsenious acid is slightly soluble in alcohol.

C. ARSENIC ACID. AsO^5.

Arsensäure, Arseniksäure, Acide arsenique.

Formation.—1. The aqueous solutions of chlorine (Bergman), bromine (Balard), and iodine (Simon, *Repert.* 65, 198), convert the metal and arsenious acid into arsenic acid. The same effect is produced by a mixture of nitric and hydrochloric acid. (Scheele.) If the mixture of hydrochloric and nitric acid is too dilute to evolve chlorine, it does not attack the arsenic till heat is applied, or a few drops of hyponitric acid added. (Millon.)—2. Strong nitric acid boiled with the metal or with arsenious acid, converts it into arsenic acid. (Thomson.) If the quantity of nitric acid is not sufficient to convert the whole of the arsenic into arsenic acid, a white powder of arsenious acid is at first produced. Dilute nitric acid, boiled with arsenic, produces a mixture of arsenious and arsenic acid. (Gm.)—3. Arsenic immersed in gaseous hypochlorous acid, or in its aqueous solution, yields arsenic acid, free chlorine, and a small quantity of chloride of arsenic; arsenious acid in aqueous hypochlorous acid, yields arsenic acid and chlorine gas; arsenic immersed in the aqueous solution of an alkaline hypochlorite loses its lustre, and forms an arseniate of the alkali. (Balard.)—4. When metallic arsenic or arsenious acid, is exploded with nitre.—5. When the metal is exploded with chlorate of potash, an effect which is brought about even by percussion.—6. When an alkaline arsenite is ignited, an arseniate of the alkali is formed and metallic arsenic is volatilized. Also when arsenious acid is heated to redness with an alkaline carbonate, arsenic acid is formed and combines with the alkali, while carbonic acid is driven off (Gay-Lussac); similarly with lime. (Wollaston).—When arsenic is heated, but not to redness, with hydrate of potash, hydrogen is evolved, and arsenite of potash, together with arsenide of potassium, produced. In consequence of the formation of the latter compound, the mass when dissolved in water, evolves arseniuretted hydrogen gas (Gehlen); if it be heated to low redness, it gives off merely the excess of arsenic; but at a higher temperature, arsenic is given off from the arsenious acid, and arseniate of potash remains behind. (Soubeiran.) Hydrate of soda exerts a similar action, but the brown mass formed by gentle heating retains a smaller quantity of arsenide of the alkali-metal, and therefore effervesces less strongly with water. Hydrate of baryta digested with arsenic gives off hydrogen, and forms a brown mass, which evolves but a small quantity of gas when treated with water, and contains nothing but arsenite of baryta. Hydrate of lime and hydrate of magnesia likewise form arsenites only, not a trace of arseniate. Also when arsenic vapour is passed over red-hot baryta or lime, a black mixture of arsenite of baryta or lime with arsenide of barium or calcium is produced; but the decomposition is very imperfect. (Soubeiran.) This statement, that lime does not form a salt with arsenic acid is in opposition to that of Wollaston above cited; perhaps Wollaston applied a stronger heat than Soubeiran.—7. Arsenite of cupric oxide is decomposed by potash, yielding cuprous oxide and arseniate of potash. (Vauquelin, *J. Pharm.* 9, 230.)

Preparation.—1·4 pt. arsenious acid is heated in a retort or in a glass flask, with 1 part of hydrochloric acid, sp. gr. 1·2, and 12 parts of nitric acid, sp. gr. 1·25—the liquid evaporated to dryness—and the residue heated to commencing redness (Bucholz.)—2. Thomson dissolves arsenic in nitric acid, evaporates to dryness, separates the resulting arsenic acid from the arsenious acid by solution in water, and again evaporates to dryness.

Properties.—Solid; after fusion, it is colourless, transparent, and glassy; after long keeping, or if it has been less strongly heated, it is white and opaque. Specific gravity = 3·391 (Bergman); 3·729 (Herapath); and 3·7342 after gentle ignition (Karsten).—Melts at a low red heat. Reddens lime strongly. Almost tasteless at first, but afterwards tastes very sharp and acid. Excessively poisonous.

			Thomson.		Proust.	Mitscherlich.
			later.	*earlier.*		
As	75	65·22	61·29	65·62	65	65·04
O^5	40	34·78	38·71	34·38	35	34·96
AsO^5	115	100·00	100·00	100·00	100	100·00

	Berzelius.	Thénard.	Bucholz.
As	65·283	65·4	72
O^5	34·717	34·6	28
	100·000	100·0	100

(As^2O^5 = 2 . 470·04 + 5 . 100 = 1440·08. Berzelius.)

Decompositions.—The aqueous solution placed in the circuit of the voltaic battery rapidly deposits arsenic [and evolves arseniuretted hydrogen?] at the negative pole, and gives off oxygen at the positive pole.—2. The dry acid, when heated somewhat above its melting point, is resolved into oxygen gas and arsenious acid, which volatilizes. The arsenic acid which remains undecomposed when the experiment is interrupted, is mixed with a small quantity of arsenious acid, some of which remains undissolved on digesting the residue in hot water, and the rest separates as the solution is evaporated (Bucholz, Richter.)—3. Hydrogen, carbon, phosphorus, sulphur, potassium, sodium, manganese, antimony, bismuth, zinc, tin, lead, iron, cobalt, nickel, copper, and likewise arsenic itself, when heated somewhat strongly with arsenic acid, either abstract the whole of its oxygen, or convert it into arsenious acid. Mercury and silver decompose this acid at very high temperatures only; gold and platinum not at all. The deoxidation is often attended with combustion, *e. g.*, when effected by potassium or sodium (Gay-Lussac & Thénard), or by iron (Scheele), or by zinc (Berzelius.)—4. The aqueous acid with zinc, tin, or iron, yields an arseniate of the corresponding metallic oxide, and arseniuretted hydrogen. Under these circumstances, iron precipitates a small quantity of arsenic in black needles; zinc precipitates it in the form of a brown powder. (Fischer, *Pogg.* 9, 261; Mohr, *Ann. Pharm.* 23, 219.)

—5. The aqueous acid placed under phosphuretted hydrogen gas soon becomes covered with a dark copper-coloured deposit, probably consisting of phosphide of arsenic. (Graham.)—6. Dry arsenic acid absorbs sulphuretted hydrogen, forming water and pentasulphide of arsenic. (A. Vogel.) When sulphuretted hydrogen is passed through aqueous arsenic acid, the liquid becomes turbid, sometimes in a few minutes, sometimes not for hours; the stronger the solution, the sooner does it become turbid; ultimately, the arsenic is completely precipitated in the form of pentasulphide, but not till the gas has been passed through the solution for a long time.

$$AsO^5 + 5HS = AsS^5 + 5HO.$$

If arsenious acid is present, the turbidity appears immediately. (*Comp.* Pfaff; Buchner, *Schw.* 45, 95, and 119.)—7. Hyposulphite of soda added to aqueous arsenic acid precipitates pentasulphide of arsenic, slowly at ordinary temperatures, quickly when heat is applied. (Himly, *Ann. Pharm.* 43, 150.)

$$5(NaO, S^2O^2) + AsO^5 = 5(NaO, SO^3) + AsS^5.$$

8. Aqueous arsenic acid mixed with sulphurous acid, quickly deposits large octohedrons of arsenious acid: this reduction is accelerated by heat. (Wöhler, *Ann. Pharm.* 30, 224.)

Combinations.—*a.* With Water.—*α. Crystallized Arsenic Acid.*—The aqueous solution sometimes deposits large and highly deliquescent crystals. (Mitscherlich.)

β. Aqueous Arsenic Acid.—Arsenic acid deliquesces slowly in the air; dissolves slowly in 6 parts of cold water, more quickly in 2 parts of hot water. On evaporating the solution, a syrupy and ultimately a turpentine-like substance is obtained, from which small crystals of arsenic acid are deposited. (Bucholz.) The solution concentrated as much as possible has, according to A. Vogel (*Kastn. Arch.* 9, 319), a density of 2·550; it contains only 40·5 parts of water to 100 parts of acid; remains liquid at — 26°; absorbs moisture from the air, whereby its density is increased to 1·935. Aqueous arsenic acid is colourless. It is very slowly precipitated by hydrosulphuric acid, the precipitate being yellow; the same result is more quickly produced by digestion for an hour with an alkaline hydrosulphate, and subsequent addition of hydrochloric acid. With baryta, strontia, or lime-water in excess, it gives a white precipitate; with an ammonio-salt of copper, pale greenish-blue; and with nitrate of silver, brown-red. With nitrate of mercurous oxide, it gives a yellowish-white, and with nitrate of mercuric oxide, a yellow precipitate. It does not change the colour of chromate or permanganate of potash.

b. With Salifiable Bases, arsenic acid forms salts called ARSENIATES. The affinity of arsenic acid for bases is much greater than that of arsenious acid. Arsenic acid, like ordinary phosphoric acid, requires 3 atoms of base to form a normal salt; moreover, like phosphoric acid, it forms salts containing 2 and 1 At. base, and having the deficient portion of base replaced by 1 or 2 At. basic water; modifications analogous to pyrophosphoric and metaphosphoric acid, it does not appear to form. The tri-acid and di-acid arseniates of the alkalis have an alkaline reaction, the mono-acid salts of the same bases, an acid reaction. Many arseniates, especially those which contain one atom of acid, are fusible. Most arseniates—provided their base is not volatile, and not disposed to abstract oxygen from the arsenic acid—sustain a red heat without decomposition;

those which contain one atom of acid however, give off a portion of their acid in the form of oxygen and arsenious acid. When ignited with charcoal, they either evolve arsenic or form a metallic arsenide. When a mixture of an arseniate with charcoal and boracic acid is heated to redness in a bulb blown at the end of a glass tube, a mirror of arsenic sublimes. When mixed with carbonate of soda and ignited on charcoal in the inner blowpipe flame, the arseniates emit the odour of garlic. Hydrogen gas likewise separates metallic arsenic from many arseniates (the zinc and the soda salt, for example) at a red heat. When the solution of an arseniate in hydrochloric acid is saturated with sulphuretted hydrogen, it gradually yields a precipitate of pentasulphide of arsenic, the precipitation being slower—sometimes going on for hours—as the solution is more dilute. If the base of the salt is likewise precipitable by sulphuretted hydrogen from an acid solution, a compound of pentasulphide of arsenic with the sulphide of the other metal is precipitated. In the case of cadmium, lead, copper, and certain other metals, the sulphide of arsenic may be dissolved out from the precipitate by dilute ammonia, and separated after filtration, by the addition of hydrochloric acid, the other metallic sulphide remaining undissolved by the ammonia; but if the other sulphide (bisulphide of tin, for example) is likewise soluble in ammonia, the ammonia dissolves both sulphides together. An alkaline hydrosulphate, with the subsequent addition of hydrochloric acid, acts in the same manner as sulphuretted hydrogen gas. An aqueous solution of an arseniate boiled with hyposulphite of soda deposits pentasulphide of arsenic on the addition of hydrochloric acid. Potash withdraws from the arseniates of the earthy alkalis, earths, and heavy metallic oxides, the greater part, if not the whole of the arsenic acid. Of the arseniates which contain 3 atoms of base to one of acid, water dissolves only those which contain the more soluble alkalis; the others are soluble only in excess of arsenic, sulphuric, hydrochloric, or nitric acid (according to the base), or in ammoniacal salts, especially in sal-ammoniac. Arseniate of silver however does not dissolve in ammoniacal salts. The solutions of the alkaline trisarseniates and diarseniates give white precipitates with baryta or lime-water, and with the salts of baryta, strontia, lime, the earths, manganous oxide, stannous oxide, zinc-oxide, lead-oxide, and ferric oxide; yellowish white with uranic and mercurous salts; yellow with mercuric salts; rose-coloured with cobalt-salts; green with nickel-salts; pale greenish-blue with cupric salts; light brown with platinic salts; and brown-red with silver salts. These precipitates are, for the most part, soluble in arsenic, sulphuric, hydrochloric, and nitric acid, and likewise in ammoniacal salts. Arseniate of potash gives a precipitate with sulphate of uranic oxide, even when so far diluted that only 1 part of arsenic acid is contained in 10,000 parts of water, and produces a slight turbidity even with 1 part of acid in 20,000 parts of water: with sulphate of zinc it gives a precipitate in 500 parts of water, and a slight turbidity in 1000 parts; with sulphate of ferrous oxide, a precipitate in 10,000 parts of water, and a very slight turbidity in 30,000 parts; with acetate of lead a precipitate after some time in 15,000 parts of water, and a very slight turbidity in 60,000 parts. (Brandes & Ebeling.) All arseniates dissolved in water or in nitric acid give with acetate of lead a white precipitate, which when heated upon charcoal before the blowpipe, fuses and emits the characteristic odour of arsenic.

ARSENIC AND HYDROGEN.

A. SOLID ARSENIDE OF HYDROGEN.

1. When a voltaic current is passed through water, and metallic arsenic is made to form the negative electrode, the arsenic becomes covered with solid arsenide of hydrogen. (H. Davy.) In repeating this experiment, Magnus, who however used but a weak battery, obtained merely a trace of the solid arsenide; and Soubeiran, from the same cause, obtained none.—2. When arsenide of potassium or sodium is dissolved in water, solid arsenide of hydrogen is left behind. (H. Davy; Gay-Lussac & Thénard.) Brown powder. Evolves hydrogen when heated, and burns on being heated in the air. (H. Davy.) Even when it has previously been heated to 100° in a current of hydrogen gas, it still gives off hydrogen when more strongly heated; and the hydrogen thus evolved is free from arsenic. (Magnus.) From Soubeiran's experiments it appears to be a diarsenide of hydrogen: AsH^2.

B. ARSENIURETTED HYDROGEN GAS. AsH^3.

Arsenwasserstoffgas, Gas hydrogène arsenié.

Formation.—1. When arsenide of potassium or sodium is treated with water, or when arsenide of zinc, tin, or iron is dissolved in dilute sulphuric or hydrochloric acid.—2. When zinc is dissolved in dilute sulphuric or hydrochloric acid with which arsenious acid is mixed. Under these circumstances, the zinc is oxidized at the expense both of the water and of the arsenious acid:

$$6Zn + 3HO + AsO^3 + 6SO^3 = 6(ZnO, SO^3) + AsH^3.$$

Iron, in place of the zinc, yields no arseniuretted hydrogen, and tin very little. (L. A. Buchner, *Repert.* 59, 234; Dupasquier, *Compt. rend.* 14, 511.) Zinc immersed in aqueous arsenious acid, without the addition of another acid, evolves no gas. (Gm.)—3. When zinc, tin, or iron is dissolved in aqueous arsenic acid, or in a mixture of that acid with hydrochloric or sulphuric acid. (Scheele.)

$$8Zn + 3HO + AsO^5 + 8SO^3 \text{ (or } AsO^5) = 8(ZnO, SO^3) \text{ or } (ZnO, AsO^5) + AsH^3.$$

Fischer (*Pogg.* 9, 261) states that aqueous arsenic acid, if not mixed with any other oxide, evolves pure hydrogen gas when treated with zinc; Gmelin, however, obtained arseniuretted hydrogen with perfectly pure arsenic acid and zinc.

Preparation.—1. An alloy of antimony with potassium and arsenic is prepared by igniting for two hours in a covered crucible, a mixture of 2 parts of sulphide of antimony, 2 parts of cream of tartar, and 1 part of arsenious acid—and afterwards reducing the product to powder and exhausting it with water. (Serullas, *J. Phys.* 98, 136.) The gas thus obtained contains very little free hydrogen. (Soubeiran.)—2. Zinc is fused with an equal weight of arsenic in an earthen retort, and the pounded alloy dissolved in a mixture of 1 part of oil of vitriol and 3 parts of water—or better, in strong hydrochloric acid. (Soubeiran.) This process yields a pure gas, whereas that obtained from arsenide of tin by the action of hydrochloric acid—and still more, that obtained from zinc and arsenic powder by hydrochloric or sulphuric acid—contains a considerable quantity of free hydrogen. (Soubeiran.) A. Vogel (*J. pr. Chem.* 6, 345) likewise obtained a perfectly pure gas by dissolving an alloy of 32·1 parts of zinc and 37·6 parts of arsenic in hydrochloric acid.—3. Zinc mixed with twice its weight of arsenious acid is dissolved in dilute sulphuric acid (Proust), or in hydrochloric acid saturated with arsenious acid, or in hydrochloric or sulphuric acid mixed with arsenic acid.

The gas may be collected over water. The most scrupulous care must be taken that not the smallest quantity be inhaled.

Properties.—Colourless gas. Specific gravity = 2·695. (Dumas.) It was formerly estimated lower, from admixture of free hydrogen. At −40°, the gas condenses to a transparent and colourless liquid, which at higher temperatures again becomes gaseous. (Stromeyer.) Does not solidify at −110° C. or −166° F. (Faraday.) Has a most repulsive and nauseating odour; kills small animals instantly, and, even when mixed with air, produces nausea, eructation, giddiness, and oppression. Excessively poisonous. Gehlen and Bullacke, who accidentally inhaled this gas, were seized, partly at once, and partly after a few days, with violent symptoms of poisoning, which, in spite of all remedial measures, terminated their lives in nine and twelve days respectively. The gas does not redden litmus.

As	75	96·15
3H	3	3·85
AsH^3	78	100·00

Or:	Vol.	Sp. gr.		Vol.	Sp. gr.
Arsenic vapour	1	10·3995	=	$\frac{1}{4}$	2·5999
Hydrogen gas	6	0·4160	=	$1\frac{1}{2}$	0·1040
Arsen. Hyd. gas	4	10·8155	=	1	2·7039

Decompositions.—1. Even the heat of a spirit-lamp is sufficient to resolve this gas into free hydrogen and metallic arsenic, which settles on the surface of the vessel. (Gay-Lussac.) One volume of arseniuretted hydrogen gas yields $1\frac{1}{2}$ vol. pure hydrogen. (Soubeiran; *Comp.* A. Vogel, *J. pr. Chem.* 6, 347.)—2. The gas, in contact with air or oxygen, may be set on fire by flame or by the electric spark. With excess of oxygen it explodes violently, giving out a white flame and forming water and arsenious acid: 1 volume of arseniuretted hydrogen consumes $1\frac{1}{2}$ vol. oxygen. (Dumas, Soubeiran.) 4 volumes of arseniuretted hydrogen contain 1 vol. arsenic vapour and 6 vols. hydrogen; 1 vol. arsenic vapour, in forming arsenious acid, takes up 3 vols. oxygen, and 6 vols. hydrogen require 3 vols. oxygen; consequently 4 vols. arseniuretted hydrogen require $3 + 3 = 6$ vols. oxygen $= 1 : 1\frac{1}{2}$. According to Stromeyer, 1 volume of arseniuretted hydrogen consumes 0·613 vols., and, according to Thénard 2 vols. oxygen; the former of these statements is explained by the presence of free hydrogen in the gas. When the quantity of oxygen is deficient, the hydrogen is first consumed, and metallic arsenic is deposited on the sides of the vessel. When set on fire in the air, the gas burns with a bluish-white flame, forming water and arsenious acid, and, if the air has not free access to it, deposits unconsumed arsenic as a metallic coating on the surface of the vessel. In contact with aerated water (Stromeyer), or when mixed with air (Soubeiran) the gas, after some time, deposits metallic arsenic. When exposed to sunlight, the gas, after a few days, deposits a black film over the whole surface of the containing vessel, whereas if kept in the dark for a week, it merely deposits a few black flakes; the arsenic, however, is not completely separated even by the action of the sun for two or three months in summer. (A. Vogel.) [If the gas were quite free from air, the light might be supposed to act like a red-heat; but if air were present, it is more probable that light would favour the oxidation of the gas: in the former case, the gas would increase in volume; in the latter, it would diminish.] In contact with anhydrous sulphuric acid, arseniuretted hydrogen liberates sulphurous acid, and deposits arsenic, which is subsequently converted into arsenic [arsenious?] acid. (Aimé, *J. Pharm.* 21, 87.) Oil of vitriol likewise decomposes the gas at ordinary temperatures, brown flakes being deposited, which are dissolved on gently heating the liquid. Oil of vitriol mixed with one part of water acts with difficulty, and when diluted with 3 parts of water, not at all. (Soubeiran.)—5. When arseniuretted hydrogen is made to flow into hypochlorous acid gas, it burns with a blue flame, forming arsenic and hydrochloric acid; and if the arseniuretted acid is not in excess, chlorine is set free. (Balard.)—6. Hyponitric and nitric acid instantly decompose arseniuretted hydrogen, oxidating the hydrogen and separating the arsenic, which also is afterwards oxidized. Fuming nitric acid produces explosion and flame. (Stromeyer.) If the pure gas be passed into a receiver filled with nitric acid, it disappears entirely, covering the sides of the vessel with a brown film. (Soubeiran.) According to Simon (*Pogg.* 41, 563), strong nitric acid has no action on the gas.

7. When chlorine is mixed with arseniuretted hydrogen, combustion ensues, the chlorine taking up the hydrogen and separating the arsenic, which, if the chlorine is in excess, is converted into chloride of arsenic, and, if water is likewise present, into arsenious and arsenic acid. (Stromeyer, Berzelius, Soubeiran.) Each bubble of chlorine, as it enters the arseniuretted hydrogen, produces a flame, and forms hydrochloric acid and a brown cloud of arsenic. (Berzelius.) From a mixture of 1 volume of arseniuretted hydrogen and 50 volumes of air or hydrogen gas, a single bubble of chlorine likewise separates arsenic, which is then deposited on the surface of the containing vessel. (A. Vogel.) If the arseniuretted hydrogen is mixed with a large quantity of carbonic acid gas, it is decomposed by chlorine without inflammation, and the separated arsenic is likewise found to be free from hydrogen. (Soubeiran.) From a mixture of arseniuretted and sulphuretted hydrogen, chlorine precipitates sulphide of arsenic. (Stromeyer.)—Chlorine-water introduced into arseniuretted hydrogen forms hydrochloric acid and arsenious or arsenic acid.—8. An aqueous solution of bromine through which the gas is passed, retains all the arsenic in the form of arsenious acid, and at the same time forms hydrobromic acid. (Simon.)—9. Iodine decomposes the gas slowly at ordinary temperatures, and quickly on the application of heat, the products being hydriodic acid and iodide of arsenic; water forms with the mixture a colourless liquid, containing the same products. (Soubeiran.) On passing the gas through an alcoholic solution of iodine, the liquid is decolorized, and only a part of the arsenic is retained in the form of arsenious acid; if the stream of gas be kept up, a small quantity of black precipitate is likewise formed. (Simon.)—10. Sulphur heated in the gas forms hydrosulphuric acid, and gives rise to the sublimation,

first of arsenic and then of sulphide of arsenic. (Gay-Lussac & Thénard, Soubeiran.)—11. Phosphorus heated in the gas till it volatilizes, produces transparent drops of phosphide of arsenic which solidify on cooling, and non-spontaneously inflammable phosphuretted hydrogen gas. —12. Heated potassium or tin (Gay-Lussac & Thénard), or zinc, (Dumas), withdraws all the arsenic from the gas, leaving pure hydrogen, the volume of which is $\frac{2}{3}$ of that of the arseniuretted hydrogen. From 1 volume of arseniuretted hydrogen, Gay-Lussac & Thénard obtained 1·37....1·55 vol. hydrogen, and Dumas 1·48. Since arseniuretted hydrogen is decomposed by the application of heat alone, and in the decomposition effected by tin, for example, part of the arsenic is separated in the free state, it does not appear that the presence of the metal is essential to the decomposition. (Soubeiran.)—13. Heated potash- or soda-hydrate quickly decomposes the gas, forming arsenite of potash, which, when more strongly heated, is converted into arseniate of potash mixed with arsenide of potassium: in this reaction, not only is the hydrogen of the arseniuretted hydrogen set free, but likewise that of the water, the oxygen of which combines with the arsenic to form arsenious acid. (Soubeiran.) The aqueous solution of potash or soda has no action on the gas.—14. Anhydrous baryta, heated in the gas, liberates the hydrogen, and is itself converted into a brownish-black mixture of arsenite of baryta and arsenide of barium. (Soubeiran.) Heated lime produces no other effect than that of heat alone. (Soubeiran.)—15. The solutions of many heavy metallic salts decompose the gas, forming water and a metallic arsenide; *e. g.*, sulphate of copper. (Soubeiran.)

$$3(CuO, SO^3) + AsH^3 = Cu^3As + 3HO + 3SO^3.$$

The blue-vitriol solution absorbs all the arseniuretted hydrogen, and leaves any pure hydrogen that may be mixed with it unaltered. (Dumas.) The condensation is very slow. (Simon.) Anhydrous sulphate of copper suffers the same decomposition; dry chloride of copper likewise yields tri-arsenide of copper and hydrochloric acid. (Kane, *Pogg.* 44, 471.)—The salts of manganese, zinc, and tin are very slowly decomposed by arseniuretted hydrogen; solution of bichloride of tin gives a yellowish brown precipitate. (Soubeiran.)—16. Dry protochloride or dichloride of mercury, with arseniuretted hydrogen gas, forms solid arsenide of hydrogen and variable quantities of hydrochloric acid gas. (Dumas.) [What becomes of the mercury?] With the aqueous solution of protochloride of mercury, the gas forms a brownish yellow precipitate, containing 1 atom of As., 6 of Hg. and 3 of Cl. (H. Rose, *Pogg.* 51, 423.)

$$6HgCl + AsH^3 = 3Hg^2Cl, As + 3HCl. \text{ (vid. \textit{Mercury}.)}$$

17. From the salts of silver, gold, platinum, and rhodium, arseniuretted hydrogen precipitates the metals, while arsenious acid remains in solution. (Soubeiran.) *e. g.*, in the case of nitrate of silver:—

$$6(AgO, NO^5) + AsH^3 = 6Ag + AsO^3 + 3HO + 6NO^5.$$

Nitrate of silver decomposes the gas completely, and with great facility. (Simon.) The precipitated silver contains a trace of arsenic. When arseniuretted hydrogen is passed through acetate of silver, the bubbles as they rise form black flakes of silver and yellow circles of arsenite of silver, which, if the stream of gas be continued, is likewise decomposed. (Lassaigne, *J. Chim. med.* 16, 685.)—Bichloride of platinum withdraws all the arsenic from the gas, and quickly forms a black precipitate, consisting of arsenic and platinum. (Simon.)—Arseniuretted hydrogen does not precipitate the salts of the alkalis, or of the earths, or of the oxides of iron (Soubeiran); neither does it precipitate tartar-emetic or sugar of lead. (Simon.)

Combinations.—Water absorbs one-fifth of its volume of arseniuretted hydrogen, and thereby acquires the property of forming dark-coloured precipitates with the above-mentioned metallic salts. (Soubeiran.)—The gas is not perceptibly absorbed by aqueous alkalis, or by alcohol or ether; but it is rapidly absorbed by oil of turpentine, and slightly by fixed oils.

On the formation and decomposition of arseniuretted hydrogen gas, is based the excellent process for detecting arsenic devised by Marsh. (*N. Ed. Phil. J.* 1826, 229; also *Repert.* 59, 220; *Phil. Mag. J.* 15, 282; 18, 441.) For the application of this process, the arsenic in the suspected substance must be in the state of arsenious or arsenic acid, or if not, it must be brought into one of those forms; it is also necessary to remove wholly or partially any organic matter that may be mixed with it, as such matter might interfere with the chemical action and produce frothing. This end is best attained by evaporating to dryness, and deflagrating the dried mass with nitre; then heating the residue with sulphuric acid and water, till all the nitric and nitrous acids are driven off; nearly saturating with potash; and decanting the solution from the crystals of sulphate of potash thereby produced;—or by deflagrating the dried residue with a mixture of 12 parts of chlorate of potash and 1 part of hydrate of potash, then dissolving in water and saturating with sulphuric acid;—or by heating the mass of animal matter with oil of vitriol or strong nitric acid till it begins to char, and then exhausting with water; or by passing chlorine in excess through water in which the whole mass is finely diffused, or through the strained decoction obtained by boiling the organic matter in water containing hydrochloric or sulphuric acid, in case the arsenic should be contained in the suspected matter, in the form of arsenious or arsenic acid;—or by digesting the whole with chloride of lime and hydrochloric acid, or with chlorate of potash and hydrochloric acid, and afterwards filtering and boiling.

¶ For the separation of the last portions of organic matter, which, if allowed to remain, are apt to produce frothing, Wöhler recommends the following process. The greater part of the organic matter having been removed by either of the methods just cited, and any excess of chlorine that may be present driven off by boiling, the arsenic is to be precipitated by passing a stream of sulphuretted hydrogen through the liquid for a day, then closing the vessel, and leaving the whole to stand for 24 hours. The precipitate, containing sulphide of arsenic with a little organic matter, is then to be collected on a small filter, and thoroughly washed: the filter, with the precipitate, introduced into a capacious porcelain crucible, and digested with strong nitric acid, till the whole is reduced to a homogeneous mass and dissolved. The excess of nitric acid is then saturated by the gradual addition of carbonate of soda; the liquid carefully evaporated to dryness; and the crucible strongly heated over a lamp till the nitrate of soda is completely fused, and the whole mass converted into a clear colourless liquid. When this point is attained, the whole of the organic matter is destroyed. The crucible is then left to cool, and the saline mass gently heated with pure concentrated sulphuric acid till the whole of the nitric and nitrous acid is driven off. The residue is then dissolved in the smallest possible quantity of water, and the solution treated in the manner about to be described. For the complete destruction of the organic matter, a considerable excess of nitrate of soda is required, a condition which may be fulfilled by using a large quantity of strong nitric acid to dissolve the sulphide of arsenic. The nitric acid and carbonate of soda must be quite free from chlorine; otherwise volatile chloride of arsenic will be formed, and occasion loss by escaping. (Wöhler, *Ann. Pharm.* 69, 367.) ¶

The liquid obtained by either of these methods—which contains in solution either arsenious or arsenic acid, and must be free from nitric and nitrous acid—is introduced, together with zinc (free from arsenic), and dilute sulphuric or hydrochloric acid (likewise free from arsenic), into a peculiar apparatus, for the purpose of developing the arseniuretted hydrogen. The apparatus may be formed of a small two-mouthed Woulfe's bottle, one aperture being fitted with an S-tube for pouring in the liquids, the other with a tube bent at right angles, for the gas to escape from. This tube may have a bulb blown on its horizontal arm, for the purpose of retaining any liquid that may be carried over with the gas, or it may be connected with a horizontal tube containing cotton or asbestos. The zinc and the dilute sulphuric or hydrochloric acid are first put into the apparatus, and after the air has been completely expelled, the operator satisfies himself that the evolved gas neither yields arsenic spots when burnt (*vid. inf.*), nor deposits a ring of arsenic when passed through a red-hot tube. This point having been satisfactorily ascertained, the liquid suspected to contain arsenic is poured through the S-tube, and the gas which afterwards comes off is examined for arsenic. (Frothing of the liquid arising from organic matter not quite removed, may be prevented by pouring in a small quantity of oil.)

The trial may be made in either of the following ways: 1. *Marsh's original process.* The gas is set on fire as it issues into the air through a glass tube drawn out to a fine point: it burns with a blue flame and deposits on a piece of glass or porcelain held close to the orifice of the jet, a brown or steel-grey spot, the *Arsenic-spot.* Mere traces of arsenic yield a great number of spots. Similar spots may however be produced in the absence of arsenic—either brown-yellow spots arising from organic matter, in case the mixture has not been properly carbonized by treatment with nitric or sulphuric acid,—or metallic spots arising from the presence of antimony. Arsenic-spots dissolve in hot nitric acid,—and if the resulting solution be evaporated to dryness and the residue dissolved in water, the liquid will give the characteristic brown red precipitate with nitrate of silver. According to Bischoff, arsenic spots are soluble in chloride of sodium; antimony spots, insoluble. The following modes of distinction may likewise be applied:

¶ *a.* Arsenic-spots exposed for ten minutes at temperatures between 12° and 15° to the action of iodine vapour, assume a pale brownish yellow colour, which however changes to lemon-yellow after a few minutes' exposure to the air. If afterwards exposed to the air for a longer time, they disappear, more quickly however when gently heated. Antimony spots, similarly treated, become dark brown, then orange-coloured by exposure to the air, and do not subsequently disappear. If the yellow spots have disappeared by exposure to moist air, they immediately reappear in the same places with a pale lemon-yellow colour on pouring a saturated solution of hydrosulphuric acid into the dish on which they are formed,—inasmuch as the arsenious acid produced by the action of the air on the iodide of arsenic, is converted by the hydrosulphuric acid into sulphide of arsenic. On touching the yellow spots with ammonia, they instantly disappear again. The spots of iodide of antimony, on the contrary, do not disappear when exposed to the air; hydrosulphuric acid converts them into orange-coloured sulphide of antimony, and when thus converted, they resist for a long time the action of dilute ammonia. An alcoholic solution of iodine immediately dissolves the arsenic spots, and, when subsequently allowed to evaporate spontaneously, leaves a lemon-yellow spot. Antimony spots are not altered by this solution; but on leaving it to evaporate in the air, the black spot of metallic antimony is converted into orange-coloured iodide of antimony. This iodide withstands a heat of 30° or 40°, and is but little altered by exposure to the air even for several days. Hydriodic acid containing free iodine may be advantageously used instead of the alcoholic solution. (Lassaigne, *Compt. rend.* 21, 1324.)

β. If a few small pieces of phosphorus be laid separate from one another in a capsule, and the capsule covered over with another on which spots have been formed by Marsh's apparatus, these spots disappear in four or five hours if they consist wholly of arsenic, whereas antimony spots similarly treated remain unaltered for a fortnight; ultimately, however, the antimony spots likewise disappear. (Cotteran, *Ann. Pharm.* 64, 420.) ¶

2. Berzelius and Liebig pass the gas through a long tube drawn out to a point and having its middle part heated to redness by a spirit-lamp or a charcoal fire. The arsenic, as it separates, is deposited towards the contracted part of the tube in the form of an arsenical mirror, which may afterwards be further examined. When the process is ended, the narrow neck may be sealed, and, after the tube has become filled with air, the deposited arsenic may be heated till it oxidizes and forms a white crystalline sublimate of arsenious acid; water may then be introduced into the tube and boiled till it dissolves the arsenious acid, and the resulting solution tested by the usual reagents.

If antimoniuretted hydrogen should be evolved together with the arseniuretted hydrogen, the antimony is deposited nearer to the hot part of the tube—generally indeed before the gas reaches the hot part—while the arsenic, being more volatile, is deposited farther off, towards the point of the tube. The antimony mirror is whiter than that formed by arsenic. If the tube be sealed at one end and heated after air has entered, the antimony mirror yields antimonic oxide; and this, when boiled with water, forms a solution which does not exhibit the characteristic reactions of arsenious acid. On passing hydrosulphuric acid gas through the tube in which, when heated to redness, arsenic and antimony have been deposited together, and, applying heat, yellow sulphide of arsenic and red and grey sulphide of antimony are formed; the former of which is more volatile than the latter (M. Pettenkofer); and if hydrochloric acid gas be then passed through, the sulphide of antimony is converted into chloride of antimony, which volatilizes, while the sulphide of arsenic remains unaltered, and may be distinguished from free sulphur by its solubility in cold ammonia. (Fresenius.)—¶ If the metallic mirror obtained as above be heated a second time while a stream of hydrogen is passed through the tube, the gas which escapes will have a strong garlic odour if the mirror contains arsenic; but none whatever if it consists wholly of antimony. Moreover, if the part of the tube at which the mirror is situated be heated to redness by the flame of a spirit-lamp, the mirror, when subsequently examined by a lens, will be found fused at the edges, and even separated into distinct shining globules, if it consists of antimony—whereas an arsenic mirror will present no such appearance, since arsenic volatilizes without fusing. (Wöhler, *Ann. Pharm.* 69, 368.) ¶

3. Danger & Flandin allow the burning gas to issue from the point of the tube into a long wide tube containing air, in which the arsenic condenses in the form of arsenious acid; instead of the tube, a funnel may also be used, or the neck of a retort separated from the body.

4. Lassaigne passes the arseniuretted hydrogen gas through a solution of nitrate of silver; precipitates the excess of silver by a small quantity of hydrochloric acid; filters; evaporates to dryness, during which process the liberated nitric acid converts the arsenious into arsenic acid; and tests the latter by the usual reagents.

5. Berzelius passes the gas through a weighed tube heated to redness, and containing finely-divided copper reduced from the oxide by hydrogen. The copper turns white at the end near the generating vessel, and its increase in weight gives the quantity of arsenic.

Arsenic and Phosphorus.

A. Phosphide of Arsenic.—A mixture of equal parts of arsenic and phosphorus placed in a flask and heated in the sand-bath to low redness yields a brownish black sublimate, which exhibits a conchoïdal black metallic fracture—is permanent in the air—and, when heated in the air, burns at first with a slight phosphorus flame, and then forms arsenious acid. (Landgrebe, *Schw.* 60, 184.)—Pelletier, by melting together phosphorus and arsenic, or by boiling phosphorus under water with metallic arsenic or arsenious acid, obtained a black shining mass, which oxidated in the air. Landgrebe regards the substance thus formed as a mere mixture.

B. Phosphate of Arsenious Acid.—Aqueous phosphoric acid dissolves arsenious acid, and unites with it, forming crystalline grains.—The two acids may be fused together into a glass.

Arsenic and Sulphur.

A. *One-sixth Sulphide of Arsenic?*—Deposited in the form of a brown powder when bisulphide or tersulphide of arsenic is boiled in solution of potash; if the potash-ley is strong, the precipitation does not take place till water is added. The powder contains, besides moisture, 96·46 per cent. of arsenic, and 3·54 p. c. sulphur. It takes fire below 100°, and burns without flame, yielding a yellow powder of sulphide of arsenic and a crystalline sublimate of arsenious acid. When heated in vacuo, it forms two sublimates; the lower of these is metallic arsenic; the upper, which amounts to about one-third of the whole, is easily fusible, translucent, and when in thin pieces exhibits a yellowish brown colour by transmitted light; black-brown by reflected light. Contains 89·5 (2 At.?) arsenic, and 10·5 (1 At.?) sulphur. (Berzelius.)

B. Bisulphide of Arsenic; Hypo-arsenious Sulphide; Hyposulpharsenious Acid.—*Red Sulphide of Arsenic, Realgar, Sandarach, Ruby Arsenic.*—Found native.—Prepared on the large scale by distilling iron pyrites with arsenical pyrites.—According to Thénard, it may be obtained by fusing arsenic with the yellow sulphide of arsenic. Crystalline system of the native variety, the oblique prismatic; *Fig.* 91 and 99, together with *h*–, *m*–, and other faces; *i*: the edges between *u* and $u' = 86°$; $u : u = 74° 30'$. Cleavage imperfect, parallel to *i*, *u*, and *t*. Specific gravity, 3·5444. (Karsten.) Colour, aurora-red, inclining to hyacinth-red and brown; often translucent; yields an orange-yellow powder, which becomes red-brown whenever it is heated. Easily fusible, rather more easily than orpiment; according to Magnus, it crystallizes on cooling. When heated out of contact of air, it volatilizes undecomposed at a temperature much below a red heat.

			Klaproth. *native.*	Laugier. *native.*	Thénard.
As	75	70·09	69	69·57	75
2S	32	29·91	31	30·43	23
AsS^2	107	100·00	100	100·00	100

Burns in the air with a blue flame, forming sulphurous and arsenious acid. With hot nitric acid it yields arsenic acid and sulphur, the latter, by further action of the nitric acid, being converted into sulphuric acid. With heated oil of vitriol, it forms sulphurous and arsenious acid. Deflagrates with nitre, producing a vivid light. The *Indian White-fire* is produced by the combustion of a mixture of 24 parts of nitre with 7 sulphur and 2 realgar. When passed together with vapour of water through a red-hot tube, realgar yields a large quantity of hydrosulphuric acid gas, and a sublimate of sulphide of arsenic and arsenious acid. (Regnault, *Ann. Chim. Phys.* 62, 384.) When boiled with aqueous solution of potash or hydrosulphate of potash, it is decomposed, yielding $\frac{1}{6}$-sulphide of arsenic and sulpharseniate of potassium which dissolves. (Berzelius.) If the bisulphide of arsenic be dissolved in the alkaline liquid when cold, the $\frac{1}{6}$-sulphide is not precipitated till the solution is boiled. (Berzelius.)

Bisulphide of arsenic combines with basic metallic sulphides forming a class of sulphur-salts, called by Berzelius, HYPOSULPHARSENITES. They contain 1, 2, or 3 atoms of a basic metallic sulphide united with 1 atom of AsS^2; *e.g.* KS,AsS^2, $2KS,AsS^2$, and $3KS,AsS^2$.—*Preparation.*—1. By fusing realgar with another metallic sulphide.—2. By fusing arsenic with a compound formed of tersulphide of arsenic and another metallic sulphide. When prepared by either of these two methods, the compound may take up an excess of sulphide of arsenic, and thereby loses its solubility in water.—3. When orpiment is boiled in a moderately concentrated solution of carbonate of potash or soda, and the colourless liquid filtered hot and then left to cool, a brown, flocculent precipitate is obtained, consisting of 1 At. bisulphide of arsenic with 2 At. monosulphide of potassium or sodium.—4. The same flakes are obtained by the spontaneous evaporation of the compounds of tersulphide of arsenic with sulphides of the alkali-metals and magnesium.—5. By precipitating the salts of the earthy alkalis, earths, and heavy metallic oxides, with a cold aqueous solution of the potassium compound. Yttrium, glucinum, and aluminum, however, do not appear to form compounds of this kind; for the red mixtures give off hydrosulphuric acid and yield light-coloured precipitates. Many heavy metals also—not manganese and zinc, however,—likewise give yellow precipitates, which cannot be distinguished from those which are formed by sulpharsenite of potassium. (Berzelius.)

The hyposulpharsenites are either red or dark brown.

Hyposulpharsenite of potassium or sodium prepared by (1) or (2) is resolved by [hot?] water into black-brown $\frac{1}{6}$-sulphide of arsenic which is precipitated, and sulpharseniate of potassium or sodium which dissolves. Hence, these hyposulpharsenites of the alkali-sulphides cannot be prepared by treating bisulphide of arsenic with the aqueous solution of a pure alkali or an alkaline hydrosulphate, because the same decomposition would ensue. Hence also, metallic arsenic is not dissolved by aqueous solutions of the alkaline sulpharsenites. The compounds of bisulphide of arsenic with 2 atoms of potassium-sulphide or sodium-sulphide are resolved in water into a soluble compound containing excess of potassium- or sodium-sulphide, and an insoluble compound of 1 At. bisulphide of arsenic with 1 At. sulphide of the alkali-metal. Most other hyposulpharsenites are insoluble in water. Aqueous acids separate bisulphide of arsenic from many of them, and liberate hydrosulphuric acid. (Berzelius.)

C. Tersulphide of Arsenic; Arsenious Sulphide (Berzelius); Sulpharsenious Acid. (Graham.)—*Yellow Sulphide of Arsenic, Orpiment, Auripigment, Operment, Resigaltum, Rauschgelb.* Found in nature. Formed by the mutual action of arsenious acid and sulphuretted hydrogen in a liquid containing a strong acid. (*Sch.* 43.) May be obtained, according to Thénard, by fusing red sulphide of arsenic with sulphur. The much more poisonous substance obtained on the large scale by subliming arsenious acid with a small quantity of sulphur, is a mixture of 6 per cent. of sulphide of arsenic with 94 of arsenious acid: the latter compound may be extracted by boiling water. (Guibourt.) The native sulphide forms crystals belonging to the right prismatic system. *Fig.* 63; *u* : *u'* = 117° 5'; easily split, parallel to *t*, into thin flexible laminæ. Specific gravity = 3·459 (Karsten), 3·48 (Mohs). Of pearly lustre; translucent; lemon-yellow inclining to orange-yellow. The powder of the native sulphide is lemon-yellow; that of the artificial variety has an orange-yellow colour, and turns brown-red whenever it is heated. Fuses easily, and, if access of air be prevented, volatilizes undecomposed; the boiling point, according to Mitscherlich, is about 700°.

			Berzelius. *artif.*	Laugier. *native.*	Klaproth. *native.*
As	75	60·98	61	61·86	62
3S	48	39·02	39	38·14	38
AsS^3	123	100·00	100	100·00	100

Exhibits the same decompositions as B. Red-hot iron or silver withdraws the sulphur from the vapour and sets the arsenic free, or, if present in excess, immediately combines with it and forms arsenide of iron or of silver. A few drops of hot nitric acid placed upon melted orpiment produce deflagration (Proust); oil of vitriol acts upon it more strongly than upon realgar. Tersulphide of arsenic deliquesces rapidly in chlorine gas, evolving great heat and forming chlorosulphide of arsenic. (H. Rose.) When boiled with water, it evolves an extremely small quantity of hydrosulphuric acid, while a trace of arsenious acid dissolves in the water. At ordinary temperatures, this action goes on for several days, but is accelerated by sulphuric or hydrochloric acid. (Decourdemanche, *J. Chim. med.* 3, 229.) Even the native sulphide undergoes this decomposition in water, but the change is never more than superficial. (Hünefeld, *J. pr. Chem.* 7, 235). When boiled with strong hydrochloric acid, it is decomposed, but with great difficulty; the hydrosulphuric acid and chloride of arsenic which are evolved, reproduce sulphide of arsenic in the receiver. (Gm.) With aqueous alkalis it forms solutions containing arsenite of the alkali and sulpharsenite of the metallic sulphide; and on boiling these solutions, a small quantity of sulpharseniate of the metallic sulphide is formed and $\frac{1}{6}$-sulphide of arsenic deposited. The vapour of arsenious sulphide passed over red-hot lime yields sublimed arsenic and sulphide of calcium, mixed with a small quantity of sulphate of lime and a large quantity of arsenite of lime, which, on the application of a stronger heat, is converted into arseniate. Red-hot magnesia shows little or no action. (Simon, *Pogg.* 40, 411, 437.) When the vapour of arsenious sulphide is passed over an ignited mixture of charcoal and carbonate of potash, or charcoal and lime, the charcoal withdraws oxygen from the alkali—the alkali-metal separates sulphur from part of the arsenious sulphide—and the sulphide of the alkali-metal thereby produced combines with the rest of the arsenious sulphide. (Liebig.) Similar results are obtained by passing hydrogen over a red-hot mixture of alkaline carbonate and arsenious sulphide. (Berzelius.) The mixture is heated in a tube drawn out to a fine point, while a current of hydrogen is passed over it. The arsenic sublimes in the contracted part. (Berzelius.) When arsenious sulphide is heated with cyanide of potassium, sulphocyanide of potassium is formed and the whole of the arsenic sublimed. To separate the arsenic, 1 part of arsenious sulphide is added to 12 parts of a mixture of 1 part of cyanide of potassium and 3 parts of dry carbonate of soda, and the whole heated to redness in a glass tube drawn out to a fine point, dried carbonic acid gas being passed through the tube during the ignition (if hydrogen were substituted for the carbonic acid, antimony, if present, might sublime together with the arsenic: *Fresenius & Babo.*) [For the behaviour of this compound when heated with litharge, *vid.* Berthier] (*Ann. Chim. Phys.* 39, 260.) Pulverized arsenious sulphide thrown into an aqueous solution of protochloride of mercury, quickly produces a white powder consisting of dichloride of mercury [or a compound of chloride and sulphide of mercury] and a solution of arsenious acid and hydrochloric acid. (Pagenstecher, *Repert.* 61, 31; 73, 14.) Arsenious sulphide when distilled, first yields a sulphide of arsenic richer in sulphur than itself, and afterwards another sulphide richer in arsenic. (Berzelius.)

Combinations.—*a.* With Water.—*Aqueous Tersulphide of Arsenic.* May likewise be regarded as *Hydrosulphate of Arsenious Acid* $= AsO^3, 3HS$.—Finely divided arsenious sulphide—that namely which is obtained by precipitating arsenious acid with sulphuretted hydrogen—after it has been washed with cold water, dissolves to a slight extent in hot water, forming a yellow solution; water containing sulphuretted hydrogen does not dissolve it. (Berzelius.)—2. Dilute arsenious acid into which hydrosulphuric gas is passed, or to which hydrosulphuric acid water is added, forms a clear yellow mixture, but gives no precipitate. It is only when hydrosulphuric acid gas is passed through a saturated aqueous solution of arsenious acid that a precipitate is immediately formed. (Bischof, *Br. Arch.* 17, 239.) The precipitation is almost complete. (Gm.) The arsenious sulphide separates from the yellow liquid in yellow flakes: (1.) When the liquid freezes. (Pfaff.)—2. When it is heated (Boutigny): in this case the precipitation is not complete. (Gm.)—3. On the addition of a small quantity of one of the stronger acids. The greatest effect is produced by sulphuric, hydrochloric, or nitric acid; then follows oxalic acid, then acetic, then tartaric acid; carbonic acid likewise appears to produce some effect. (Boutigny.)—4. On the addition of certain salts, *e. g.* sal-ammoniac, nitre, sulphate of soda, and sulphate of magnesia. (Boutigny, *J. Chim. med.* 8, 449.) The aqueous mixture of arsenious acid and hydrosulphuric acid when kept for weeks in a stoppered bottle deposits but little arsenious sulphide. (Gm.) ¶ According to H. Becker (*Pogg.* 74, 303) arsenic, whether in the state of arsenious or arsenic acid, can never be completely precipitated from its solutions, either by hydrosulphuric acid or by alkaline hydrosulphates. The quantity of arsenic which remains in the liquid may however be rendered utterly insignificant (excepting for judicial investigations) by adopting the precaution: (1) of placing the liquid, after saturation with hydrosulphuric acid, in a nearly air-tight vessel, and leaving it in a warm place for 6 or 8 days; (2) saturating it anew from time to time with hydrosulphuric acid (because, if the saturation be not complete, the acid liquid redissolves a portion of arsenic from the arsenious sulphide); and (3) filtering the liquid from the precipitate before driving off the excess of hydrosulphuric acid. ¶

b. With Basic Metallic Sulphides, forming a class of sulphur-salts, called SULPHARSENITES.—Combination takes place in three different proportions: *e. g.*, in the case of potassium: $3KS,AsS^3$; $2KS,AsS^3$; KS,AsS^3; forming respectively *terbasic* or *tris-acid*, *bibasic* or *di-acid*, and *monobasic*, or *mono-acid* sulpharsenites. [The first of these must be regarded as the normal salt.]

Preparation.—1. By depriving sulpharseniates, (that is, sulphur-salts containing pentasulphide of arsenic) of part of their sulphur, by igniting them out of contact of air.—2. By dissolving tersulphide of arsenic in a warm aqueous solution of the protosulphide of an alkali-metal, or of the double sulphide of hydrogen and the metal (alkaline monohydrosulphate or bihydrosulphate). The solution in aqueous sulphide of ammonium is attended with some rise of temperature (H. Rose.) When an alkaline bihydrosulphate is used, half of the hydrosulphuric acid is expelled. When complete saturation is attained, one atom of orpiment dissolves in one atom of ammonium-, potassium-, or sodium-sulphide, and in 2 atoms of barium-, strontium-, calcium-, or magnesium-sulphide.—3. By dissolving orpiment in a cold aqueous solution of an alkali. Under these circumstances, part of the alkali is converted into arsenite of potash, which remains mixed with the sulpharsenite: *e. g.*

$$4AsS^3 + 5KO = 3(KS,AsS^3) + 2KO,AsO^3.$$

Hence, when this solution is mixed with one of the stronger acids, no sulphuretted hydrogen is evolved, but the whole of the arsenic is separated in the form of arsenious sulphide:

$$3(KS,AsS^3) + 2KO,AsO^3 + 5SO^3 = 5(KO,SO^3) + 4AsS^3.$$

If the solution first obtained were heated with excess of tersulphide of arsenic, that compound would be converted into bisulphide, and the sulpharsenite of potassium into sulpharseniate.—4. By dissolving arsenious acid in the aqueous solution of an alkaline bihydrosulphate. If bihydrosulphate of ammonia be used, half of the ammonia remains in the liquid in the free state:

$$2(NH^3,2HS) + AsO^3 = NH^4S,AsS^3 + NH^3 + 3HO.$$

When the potassium compound is used, half of the potash is converted into arsenite:

$$2(KS,HS) + 2AsO^3 = KS,AsS^3 + KO,AsO^3 + 2HO.$$

5. The compounds of sulpharsenious acid with the sulphides of the earth-metals and heavy metals are obtained by precipitating a solution of the corresponding compound of an alkali-metal, obtained by either of the methods 2, 3, 4, with a salt of the earth-metal or heavy metal. (Berzelius.)

The sulpharsenites are either yellow or red. Most of them, when ignited out of contact of air, give off all their sulphur-acid; others give up such a quantity that the residue contains 3 At. sulphur-base to 1 At. sulphur-acid; but the sulpharsenites of the alkali-metals, even those which contain equal numbers of atoms of base and acid, give off nothing when ignited. The alkali-metal compounds obtained by the first method, when treated with a small quantity of water—and the dilute solutions obtained by method 2, 3, or 4, when they evaporate in the air—are resolved into brown hyposulpharsenite which is precipitated, and sulpharseniate which remains in solution; but the decomposition is not complete, till the solution is concentrated to the crystallizing point of the latter salt. If the decomposed mass be digested in a large quantity of water and boiled, the whole is reconverted into sulpharsenite and redissolved. The solutions of the barium, strontium, calcium, and magnesium salts, containing 1 As. base to 1 At. acid, deposit, on boiling, a portion of the arsenious sulphide; the ammonium, potassium, sodium, and lithium compounds remain undecomposed. On adding alcohol to the aqueous solution of a compound of 1 atom of arsenious sulphide with 2 atoms of the sulphide of an alkali-metal, a compound containing 3 atoms of sulphur-base is precipitated, while a compound containing 1 atom of sulphur-base remains in solution:

$$2(2KS,AsS^3) = 3KS,AsS^3 + KS,AsS^3.$$

But the precipitated terbasic salt soon turns black, being resolved into hyposulpharsenite and sulpharseniate. The potassium and sodium compounds exhibit this blackening on the addition of alcohol, even when the solution contains nothing but terbasic salt ($3KS,AsS^3$); but with the ammonium, barium, strontium, and calcium salts, it does not take place unless the solution contains bibasic salt ($2BaS,AsS^3$).—Aqueous solutions of sulpharsenites exposed to the air are decomposed by oxidation (more slowly in proportion to the excess of sulphur-base), depositing orpiment and a brown compound of bisulphide of arsenic with the sulphur-base. Hydrated oxide of copper, added to a solution containing a compound of sulpharsenious acid with the sulphide of an alkali-metal, decomposes that compound, yielding twelve-basic sulpharsenite of copper, which remains undissolved, and a hyacinth-red solution, containing an alkaline arsenite and terbasic sulpharsenite of copper, and deposits the latter on the addition of hydrochloric acid. Probably thus:

$$9(KS,AsS^3) + 27CuO = 2(12CuS,AsS^3) + 3CuS,AsS^3 + 9KO,6AsO^3.$$

If the hydrated oxide of copper is in excess, the arsenious acid contained in the solution is converted into arsenic acid, and the protoxide of copper reduced to di-oxide. Oxide of silver in excess decomposes the solution, forming sulphide of silver and alkaline arsenite:

$$KS,AsS^3 + 4AgO = 4AgS + KO,AsO^3.$$

Acids added to these solutions precipitate arsenious sulphide, and resolve the sulphide of the alkali-metal into an alkaline salt and hydrosulphuric acid gas. (Berzelius.)

The only sulpharsenites which are soluble in water are those which contain the sulphides of the alkali-metals or of magnesium; and even these are decomposed by water, unless the water is in considerable quantity (p. 276). Hence the solution cannot be evaporated to dryness to obtain the dry salt, without undergoing decomposition. The solution is colourless—or yellowish, if it contains a large quantity of sulpharsenious acid; its taste is hepatic at first, but afterwards most disgustingly bitter. (Berzelius.) It may be supposed to contain a compound of an alkaline hydrosulphate with hydrosulphate of arsenious acid; *e. g.*

$$KS, AsS^3 + 4HO = KO, HS + AsO^3, 3HS.$$

D. PENTASULPHIDE OF ARSENIC; ARSENIC SULPHIDE (Berzelius); SULPHARSENIC ACID (Graham).—Formed in the decomposition of arsenic acid by hydrosulphuric acid—a reaction which takes place the more slowly, as the solution of arsenic acid is more dilute. (*Sch.* 44.)—*Preparation.*—1. Hydrosulphuric acid gas is passed for several days through a not very dilute solution of arsenic acid, till the liquid, after being kept in a stoppered bottle for 24 hours, still smells of the gas.—2. Aqueous arsenic acid or arseniate of potash is mixed with bihydrosulphate of potash, or aqueous arseniate of potash is saturated with hydrosulphuric acid gas, and after the solution has stood for an hour, the pentasulphide of arsenic is precipitated by hydrochloric acid. (Berzelius.)

Lemon-yellow powder, lighter than the tersulphide, and without any tinge of red. Fuses less easily than sulphur, and after fusion appears darker and somewhat reddish. Sublimes unchanged in the form of a red-brown viscid mass, which, after cooling, appears transparent and pale yellowish red. In the state of fine powder, it reddens tincture of litmus at a boiling heat, but not in the cold, though the hot liquid remains slightly red after cooling; it likewise imparts a transient redness to litmus-paper on which it is laid, provided the vapour of boiling water is also brought in contact with the paper. (Berzelius.) If a solution of arsenic sulphide in ammonia be precipitated by nitrate of silver, and nitric acid cautiously added to the filtered liquid till the ammonia is neutralized, a red-brown precipitate of arseniate of silver is thrown down; arsenious sulphide treated in the same manner gives a yellow precipitate of arsenite of silver. (H. Rose.)

As	75	48·39
5S	80	51·61
AsS^5	155	100·00

In the unfused state, it yields a small quantity of sulphur to boiling alcohol, and becomes darker in colour. Dissolves easily, with partial decomposition (*vid. inf.*) in aqueous solutions of the pure fixed alkalis and of their hydrosulphates and carbonates, driving out the carbonic acid from the latter on the application of heat. Dissolves completely in concentrated aqueous ammonia, but if digested in more dilute ammonia, leaves a residue of sulphur. Not soluble in boiling water.

Towards basic metallic sulphides, pentasulphide of arsenic plays the part of an acid, and forms with them a class of sulphur-salts, called SULPHARSENIATES. In these salts, 1 atom of arsenic sulphide is combined with 1, 2, or 3 atoms of the basic sulphide; *e. g.*, KS, AsS^5; $2KS, AsS^5$; $3KS, AsS^5$; so that, in this case also, we have to distinguish between *monobasic*, *bibasic*, and *terbasic* salts.—*Preparation.*—1. By dissolving pentasulphide of arsenic in a warm solution of an alkaline monohydrosulphate or bihydrosulphate. In the latter case, the second atom of hydrosulphuric acid is driven off, with brisk effervescence. The solution contains a bibasic salt; *e. g.*, $2KS, AsS^5$. It is only by longer digestion with excess of the pentasulphide, that a larger quantity of it is dissolved, and in that case, the quantity taken up increases with the temperature and concentration of the liquid; part of it is, however, precipitated as the liquid cools, so that ultimately, not more than $\frac{3}{7}$ At. sulpharsenic acid remains dissolved, in combination with 1 At. sulphur-base.—(Pentasulphide of arsenic being a stronger acid than the tersulphide, its solution in hydrosulphate of ammonia is attended with greater rise of temperature than that of the tersulphide: *H. Rose.*)—2. By passing hydrosulphuric acid gas through the aqueous solution of an alkaline arseniate—whereupon, the gas is absorbed slowly at first, but afterwards more quickly—till the liquid no longer gives a precipitate with chloride of barium or calcium:

$$2KO, AsO^5 + 7HS = 2KS, AsS^5 + 7HO.$$

Or by mixing the solution of an alkaline arseniate with excess of bihydrosulphate of ammonia, and distilling till the free ammonia and excess of hydrosulphate of ammonia are expelled.—3. If the arseniate used is insoluble in water, that of copper, for example, it must be dissolved in hydrochloric acid, and the sulpharseniate of copper precipitated by sulphuretted hydrogen.—4. By fusing pentasulphide of arsenic with a pure caustic alkali, or with its hydrate or carbonate. Under these circumstances, arsenic sublimes, and the sulphur-salt produced is mixed with arseniate and sulphate of the alkali.—5. By dissolving the pentasulphide in caustic alkali (or in alkaline carbonate at a boiling heat, the carbonic acid being then driven off.) In this case, an alkaline arseniate is always formed at the same time. Probably in this manner:

$$14KO + 7AsS^5 = 5(2KS, AsS^5) + 2(2KO, AsO^5).$$

Consequently, this solution evolves no hydrosulphuric acid when the arsenic sulphide is precipitated by a stronger acid:

$$5(2KS, AsS^5) + 2(2KO, AsO^5) + 14SO^3 = 14(KO, SO^3) + 7AsS^5.$$

6. By digesting orpiment in an aqueous solution of bisulphide, or a higher sulphide of potassium; in the latter case, the excess of sulphur is precipitated.—7. The compounds of sulpharsenic acid with sulphides of certain of the earth-metals and heavy metals, are obtained by precipitating a salt of one of these metals with solution of sulpharseniate of potassium. Magnesium, yttrium, glucinum, and some of the heavy metals, however, yield soluble compounds. (Berzelius.)

The dry compounds of the alkali-metals are lemon-yellow; the others red or brown. They are permanent in the air; taste—in so far as they are soluble—first hepatic, and afterwards most intensely bitter. The terbasic salts have a tendency to crystallize; the bibasic and monobasic salts have not.

The terbasic sulpharseniates of potassium, sodium, lithium, and barium may, if air be excluded, be heated almost to whiteness without decomposing; on cooling they solidify to a yellow mass, perfectly soluble in water. The bibasic and monobasic sulpharseniates of these metals give off sulphur when heated, and are converted into sulpharsenites. The silver and mercury salts (the latter of which sublimes) remain undecomposed at a red heat. The other bibasic and monobasic sulpharseniates are decomposed by ignition, first yielding sulphur and a red salt of sulpharsenious acid; and in many cases, the sulpharsenite is resolved by continued ignition into sulpharsenious acid which sublimes, and the sulphur-base which remains behind. The calcium and magnesium salts first evolve sulphur, and then the greater part of the sulpharsenious acid, and leave a white unfused compound of magnesium- or calcium-sulphide, with a very small quantity of sulpharsenious acid; most of the heavy metal compounds evolve sulphur at first, and then all the sulphide of arsenic, so that nothing but the sulphur-base remains behind. The sulpharseniates, when heated in the air, give off orpiment and arsenious acid, and leave a sulphate when the base contains an alkali-metal, and pure oxide if it contains a heavy metal. The aqueous solution of the sulpharseniate of an alkali-metal is decomposed by exposure to the air—the liquid becoming turbid, and depositing sulphur, sulpharsenic acid, and a brown salt of hyposulpharsenious acid, while alkaline arsenite and hyposulphite are formed, and the latter, by further oxidation, is converted into sulphate; the cooler and more concentrated the solution, the more slowly does the decomposition proceed. Acids, even carbonic acid, decompose the alkaline sulpharseniates, separating hydrosulphuric acid gas of a peculiar odour, and precipitating pentasulphide of arsenic. Hydrate of cupric oxide, introduced into the solution of an alkaline sulpharseniate, decomposes a portion of that compound, forming alkaline arseniate and sulphide of copper; the latter combines with a small portion of undecomposed arsenic sulphide, forming a compound which is insoluble in water, but nevertheless dissolves partially in the liquid, provided that this liquid still contains undecomposed alkaline sulpharseniate—while sulphide of copper, containing little or no sulphuric acid, remains behind. A similar reaction is produced by other heavy metallic oxides which do not retain their oxygen with very great force. (Berzelius.)

Many sulpharseniates are soluble in water, namely, those of the alkali-metals, magnesium, yttrium, and glucinum. The solutions are either colourless or pale yellow. From the solutions of the bibasic salts, alcohol precipitates a terbasic salt, leaving a monobasic salt in solution. When this solution is placed in a shallow dish, and evaporated at a gentle heat, there remains a lemon-yellow residue, from which water extracts a bibasic salt, while arsenic sulphide is left behind, and is but partially dissolved by continued digestion. When the above-mentioned alcoholic solution is heated in a retort to the boiling point, it deposits half the arsenic sulphide which it contains, but at the same time resolves it into two other compounds, viz., tersulphide of arsenic in the form of a reddish powder, and octodeca-sulphide of arsenic in the form of pale yellow scales. (Berzelius.)

E. Octodeca-sulphide of Arsenic.—1. Obtained by precipitating the solution of bibasic sulpharseniate of potassium with alcohol, distilling $\frac{1}{2}$ or $\frac{2}{3}$ of the alcohol from the filtrate, and leaving the solution to crystallize by slow cooling.—2. A still larger quantity of this compound is obtained by digesting orpiment with an alcoholic solution of potash-liver of sulphur. Delicate pale yellow scales and fibres. (Berzelius.)

	Calculation.		Berzelius.
As	75	20·66	20·61
18S	288	79·34	79·39
AsS^{18}	363	100·00	100·00

F. Persulphide of Arsenic.—Arsenious acid may be fused with any excess whatever of sulphur; sulphurous acid is evolved, and a brownish yellow sulphide of arsenic formed, which on cooling after fusion, remains soft for a long time: its powder is yellow, the brightness of the colour increasing with the quantity of arsenic. On distilling a compound of this nature, sulphur passes over, accompanied by a continually increasing quantity of arsenic. (Berzelius.) Much of the ordinary sulphur of commerce is really a compound of this nature.

¶ G. Sulphoxiarsenic Acid.—AsO^3S^2.—When hydrosulphuric acid gas is rapidly passed through a cold saturated solution of bi-arseniate of potash, pentasulphide of arsenic is first precipitated, and afterwards a white salt is deposited. After this deposition has gone on for some time, a small quantity of caustic potash is added, and hydrosulphuric acid again passed through till the sulphide of arsenic acquires a grey colour. If the liquid be then filtered and evaporated in vacuo, crystals are obtained, which may be freed from adhering sulphide of arsenic by washing with water. These crystals consist of *Sulphoxiarseniate of potash*, KO,AsO^3S^2+2HO (vid. p. 294). When the aqueous solution of this salt is mixed with a lead salt, a white precipitate is obtained, which, however, soon turns black. On suspending this precipitate in water, adding a few drops of sulphuric acid, and filtering, an acid liquid is obtained, which does not precipitate baryta-salts, but quickly decomposes and yields a deposit of sulphur. The acid thus formed may be regarded as arsenic acid, in which 2 atoms of oxygen are replaced by sulphur. (Bouquet & Cloez, *N. Ann. Chim. Phys.* 13, 44; *J. Pharm.* 7, 23; abstr. *Ann. Pharm.* 56, 216.) ¶

H. Sulphate of Arsenious Acid.—Oil of vitriol heated with arsenic gives off sulphurous acid, and leaves a residue which forms a milky precipitate with water, and contains arsenious but no arsenic acid. —Three parts of boiling oil of vitriol dissolve 1 part of arsenious acid; of this the greater part crystallizes out on cooling, and a further portion may be precipitated by absolute alcohol; a small quantity, however, still remains dissolved. When the solution of arsenious acid in oil of vitriol is distilled, the sulphuric acid passes over quite free from arsenic, and the arsenious acid remains behind, not converted into arsenic acid. (A. Vogel. *J. pr. Chem.* 4, 232.) According to Wackenroder, part of the arsenious acid does pass over with the sulphuric acid in distillation. According to Bucholz (*Beitr.* 1, 61), the residue contains a small quantity of arsenic acid.

Arsenic and Selenium.

Selenide of Arsenic.—Selenium in the state of fusion gradually dissolves arsenic, forming with it a black, easily fusible mass, which boils at a red heat, and appears to give off a perselenide of arsenic; afterwards the boiling ceases, and no further change takes place till the heat is raised nearly to whiteness, at which temperature the entire compound distils over in drops, which solidify in a brown-black shining mass, having a conchoidal fracture. (Berzelius.)

ARSENIC AND IODINE.

A. TERIODIDE OF ARSENIC.—Arsenic powder very gently heated with iodine powder combines with it, producing great rise of temperature.—*Preparation.*—1. By heating a finely divided mixture of 16 parts of arsenic and 100 parts of iodine till it fuses. The compound thus formed contains excess of iodine. (Plisson.)—Thomson gently heats 75·2 parts (1 At.) of arsenic with 630 parts (5 At.) of iodine, and obtains the same compound; for this reason, he regards it as penta-iodide of arsenic. [Was part of the iodine driven off by the heat?]—By heating a mixture of arsenic and excess of iodine in a retort, till sublimation or distillation takes place. (Plisson.) Serullas & Hottot distil 1 part of arsenic in a retort with 3 parts of iodine. Bette sublimes 1 part of arsenic with 3 parts of iodine in a glass flask, and as the sublimate often falls down again, allows the flask to cool from time to time in order to remove the sublimate; when the sublimation takes place in vessels containing air, a small quantity of arsenious acid becomes mixed (according to Bette), with the sublimed iodide.—3. Three parts of pulverized arsenic are heated with 10 parts of iodine and with water, till the liquid no longer smells of iodine, and retains merely a pale yellow colour; it is then filtered from undissolved arsenic, and left to evaporate in the sunshine till the iodide of arsenic crystallizes out. As soon as the crystals have become tolerably dry, they are melted in a flask to drive off the water which adheres to them. (Plisson.) On dissolving the fused mixture of 1 part of arsenic and 3 parts of iodine in water, and evaporating the yellowish red filtrate to dryness over a water-bath, white and violet vapours are given off, and there remains a brick-red powder consisting of iodide of arsenic, which, however, is mixed with arsenious acid, and, when exposed to the air, evolves iodine, and turns brown-red. (Bette.)—4. The mixture obtained by fusing the arsenic and iodine together, is dissolved in hot alcohol, and filtered from the arsenious acid which separates from it; the yellowish red filtrate is then cooled down the crystallizing point, and the red laminæ which crystallize out, are dried between folds of bibulous paper frequently changed, till they no longer smell of iodine. By this process, the compound is obtained pure, but in small quantity: the black-brown mother-liquid, which contains free hydriodic acid, deposits nothing when left to itself. (Bette.) ¶ 5. Meurer passes pure arseniuretted hydrogen gas (prepared from arsenide of zinc and hydrochloric acid) through a freshly prepared alcoholic solution of iodine, but only till the liquid is decolorized. On evaporating the solution, iodide of arsenic separates in crystals. (*Arch. Pharm.* 2nd series, 52, 1.) ¶

Properties.—By method (1): brick-red mass, with crystalline fracture (Plisson); red-brown, with violet fracture (Bette); by (3): small red crystals, which assume a darker colour on drying (Plisson); by (2) and (4): light brick-red, shining laminæ. Fuses when heated, and afterwards sublimes, with slight decomposition, in yellow vapours which condense in scales. Inodorous. (Plisson.) Tastes somewhat metallic. (Thomson.)

			(2, *a*)	(2, *b*)	(3)	(4)
As	75	16·56	15·9	15	16·4	17·40
3I	378	83·44	84·1	85	83·6	82·34
AsI^3	453	100·00	100·0	100	100·0	99·74

The numbers refer to the modes of preparation; 2, *a* is iodide of arsenic obtained by sublimation; 2, *b* is the same sublimed a second time. The specimen 4 was half a year old, and had given off some of its iodine.

Decompositions.—During sublimation, a very small portion of the compound is resolved into free iodine and arsenic, and the latter, if the air has access to it, is converted into arsenious acid. (Plisson.) If the heat be suddenly raised to 138°, more complete decomposition ensues. (Thomson.)—When kept in glass-vessels which are frequently opened, it loses a portion of its iodine in the course of a few months, without, however, changing colour. (Bette.)—3. When evaporated with nitric acid, it leaves all the arsenic in the form of arsenic acid. (Plisson.)—4. Iodide of arsenic treated with a small quantity of cold water, is resolved into the acid compound C which dissolves, and the basic compound B which separates in scales. A small quantity of hot water dissolves it, but on cooling, it is decomposed in the same manner. (Plisson.)

Aqueous Teriodide of Arsenic, or *Aqueous Hydriodate of Arsenious Acid.*—Iodide of arsenic dissolves perfectly in considerable quantities of cold water, either without change of composition, or as a compound of hydriodic acid with arsenious acid: $AsI^3 + 3HO = AsO^3 + 3HI$. The yellow solution reddens litmus strongly. It does not (like free hydriodic acid) turn brown in the air, neither does it evolve iodine; hence it does not impart a blue colour to starch-paper suspended over it, except on the addition of hydrochloric acid. Hence it appears, that the hydriodic acid, if it exists in the solution, is in combination with the arsenious acid. When the liquid is boiled in a retort, iodide of arsenic remains behind, and the aqueous vapour carries with it a small quantity of that compound, but no free iodine or free hydriodic acid. By free evaporation in an open vessel, on the contrary, the solution is resolved into scales of the basic compound B, and a mother-liquid containing the acid compound C. Sulphuric and nitric acid added to the solution precipitate iodine; hydrosulphuric acid precipitates tersulphide of arsenic. The solution gives a brown precipitate with nitrate of bismuth, yellow with acetate of lead, green with ammonio-sulphate of copper; none with sulphate of lime. (Plisson, *Ann. Chim. Phys.* 39, 265; also *Pogg.* 14, 608.)

B. Arsenite of Teriodide of Arsenic.—Produced in the decomposition of teriodide of arsenic with a small quantity of water. With cold water, the separation takes place immediately; with hot water, not till the solution cools. The compound is prepared by saturating hot water with iodide of arsenic, and leaving the solution to cool slowly. (Plisson.) To free the crystalline scales from adhering acid mother-liquid, they must be washed with a small quantity of water, or better with alcohol, in which they are much less soluble. (Serullas & Hottot.) When the white scales thus obtained are gently heated, they give off their water, and are converted into a yellow powder, which, if the heat be increased, yields a sublimate of teriodide of arsenic with a small quantity of arsenious acid, while the greater part of the arsenious acid remains behind. The residue has a greyish tinge, probably from admixture of metallic arsenic. (Plisson.) The scales, if well washed with alcohol, and afterwards strongly heated, give off a considerable quantity of metallic arsenic, together with teriodide of arsenic, but without any violet vapour or arsenious acid. (Serullas & Hottot.) [The separation of metallic arsenic is probably due to the alcohol.] This compound retains a portion of water, even when heated till decomposition commences. (Serullas.)—The scales are large, white, shining, and permanent in the air. (Plisson.) It is only when some of the acid mother-liquid still adheres to them, that they turn red in the air. (Serullas & Hottot.) They contain water of crystallization, which they do not give off, even in vacuo over chloride of calcium. Hence they may likewise be regarded as a compound of 3 atoms of hydriodic acid with more than 1 atom of arsenious acid.—The scales dissolve more readily in hot water than in cold, and crystallize from the hot solution as it cools; but on each successive crystallization, the proportion of hydriodic acid diminishes and that of arsenious acid increases, so that no definite combining proportion can be made out. After very long washing with alcohol, the scales leave only 1·25 per cent. iodine and 98·75 per cent. arsenious acid. (Plisson.)—The aqueous solution of the scales behaves with sulphuric acid, nitric acid, hydrosulphuric acid, and heavy metallic salts, just like the solution of teriodide of arsenic. (Plisson.) The scales are but slightly soluble in cold water, and still less soluble in alcohol. (Serullas & Hottot.)

C. *Hydriodate of Teriodide of Arsenic*, or *Acid Hydriodate of Arsenious Acid.*—Contained in the aqueous solution which remains after the separation of the scales B, in the decomposition of teriodide of arsenic by a small quantity of water. (Plisson.) The reddish, highly acid liquid may be decomposed by repeated distillation into free hydriodic acid and the scales B. (Serullas & Hottot.)

D. *Aqueous Penta-iodide of Arsenic*, or *Aqueous Hydriodite of Arsenious Acid?*—The aqueous solution of teriodide of arsenic dissolves a large quantity of iodine. The solution, when evaporated in vacuo over oil of vitriol, first deposits acute octohedrons of iodine, and afterwards the scales B. (Plisson.)

On the relations between iodine and arsenic compare Plisson (*J. Pharm.* 14, 46; *Ann. Chim. Phys.* 39, 265; also *Schw.* 55, 335; *J. Pharm.* 14, 592). Serullas & Hottot (*J. Pharm.* 14, 49, 163, 165, and 598). Serullas (*Ann. Chim. Phys.* 38, 319; also *Schw.* 55, 345). Todd Thomson (*Repert.* 67, 360). Bette (*Ann. Pharm.* 33, 349.)

ARSENIC AND BROMINE.

A. TERBROMIDE OF ARSENIC.—Arsenic takes fire as soon as it comes in contact with bromine, burning with great brilliancy, and giving off dense fumes. To prepare the bromide, bromine is put into a retort and dry arsenic powder introduced through the tubulure in successive small portions, agitating each time, till the combustion ceases; the bromide of arsenic is afterwards distilled from the excess of arsenic. The distillate crystallizes on cooling, and forms a white fibrous mass, which, between 20° and 23°, fuses to a translucent pale-yellow liquid, boils at 220°, and in the fused state, fumes but slightly in the air. It absorbs moisture from the air, and, in contact with water, is instantly resolved into a solution of a small quantity of arsenious in a large quantity of hydrobromic acid, and the compound B which is precipitated. (Serullas, *Ann. Chim. Phys.* 38, 319; also *Schw.* 55, 345.)

Calculation, according to Serullas.

As	75·0	24·18
3Br	235·2	75·82
$AsBr^3$	310·2	100·00

B. Arsenite of Bromide of Arsenic.—Precipitated in the decomposition of bromide of arsenic by water. Retains water even when heated to incipient decomposition, and consequently, when more strongly heated, gives off water, as well bromide of arsenic and arsenious acid. Hence it may likewise be regarded as a compound of 3 atoms of hydrobromic acid with more than one atom of arsenious acid. When repeatedly washed with water (or better with alcohol), which dissolves less of the arsenious acid, it gives off all its bromine in the form of hydrobromic acid, so that nothing but arsenious acid remains behind. (Serullas.)

Arsenic and Chlorine.

A. Terchloride of Arsenic.—*Arsenic-butter*, *Caustic Oil of Arsenic.* —1. Arsenic powder thrown into chlorine gas at ordinary temperatures, burns with a reddish white light, forming white vapours of chloride of arsenic.—2. It decomposes chloride of mercury at high temperatures, abstracting the chlorine.

Preparation.—Dry chlorine gas is passed into a tube-funnel containing pounded arsenic, and having its beak turned down and inserted into a receiver containing ice. The distillate is freed by rectification over arsenic from any excess of chlorine that it may contain. (Dumas.)—2. By distilling a saturated solution of arsenious acid in concentrated hydrochloric acid with oil of vitriol. (J. Davy.)—3. By distilling arsenious acid with common salt and oil of vitriol. (Gm.) Dumas heats in a retort 40 grammes of arsenious acid with 400 grammes of oil of vitriol, at a temperature between 80° and 100°, and introduces pieces of fused common salt from time to time through the tubulure of the retort. Little or no hydrochloric acid is evolved; dry chloride of arsenic passes over first, and afterwards the hydrated compound, which forms a separate stratum in the receiver above the dry chloride; the hydrated chloride may be rendered anhydrous by repeated distillation with a large quantity of oil of vitriol.—4. By distilling one part of arsenic, at a gentle heat, with 6 parts of protochloride of mercury.

Transparent, colourless, oily, and very heavy liquid; does not solidify even at −29°. (J. Davy.) Boils at 132°. Specific gravity of the vapour = 6·3006. (Dumas.) Evaporates in the air at ordinary temperatures, producing white fumes. (J. Davy.) Highly poisonous.

	Calculation.		J. Davy.
As	75·0	41·39	39·52
3Cl	106·2	58·61	60·48
$AsCl^3$	181·2	100·00	100·00

	Vol.	Sp. gr.		Vol.	Sp. gr.
Arsenic vapour	1	10·3995	=	$\frac{1}{4}$	2·5999
Chlorine gas	6	14·7258	=	$\frac{3}{2}$	3·6814
Chlor. arsen. vapour	4	25·1253	=	1	6·2813

Antimony, bismuth, zinc, cadmium, tin, lead, iron, and copper, immersed in chloride of arsenic, become covered with a crust of metallic arsenic, which prevents further decomposition. (Fischer, *Pogg.* 9, 261.) Mercury likewise, at ordinary temperatures, decomposes chloride of arsenic very slowly, forming a greyish brown powder. (Dumas, *Ann. Chim. Phys.* 38, 337; also *Pogg.* 9, 313.)

Chloride of arsenic dissolves phosphorus at a gentle heat, without becoming luminous, and deposits it again almost completely on cooling. When heated, it dissolves sulphur in almost all proportions, but the sulphur is almost wholly precipitated on cooling. It absorbs 10 times its volume of phosgene gas, which is again evolved on mixing the liquid with water. Dissolves oil of turpentine, olive oil, and colophony. (J. Davy, *Schw.* 10, 332.)

Hydrated Terchloride of Arsenic or Terhydrochlorate of Arsenious Acid.—1. Formed by mixing chloride of arsenic with a small quantity of water: $AsCl^3 + 3HO = AsO^3 + 3HCl$.—2. In the distillation of chloride of arsenic as in (3) p. 284.—3. By dissolving arsenious acid in strong hydrochloric acid.—Transparent, colourless, heavy liquid, lighter but more viscid (according to Dumas) than chloride of arsenic. On the addition of a larger quantity of water, it is resolved, like the anhydrous chloride, into arsenious acid, which is precipitated, and dilute hydrochloric acid, containing a small quantity of either chloride of arsenic or arsenious acid in solution. The same liquid is obtained on dissolving arsenious acid in dilute hydrochloric acid. A solution of this nature, if it contains a large excess of hydrochloric acid, evaporates completely, without leaving arsenious acid behind. (Dupasquier.) If therefore hydrochloric acid containing arsenious acid in solution be distilled, the distillate contains arsenic. Similarly, when common salt is distilled with sulphuric acid which contains arsenious acid, the hydrochloric acid obtained is likewise contaminated with arsenic. (Dupasquier, *J. Pharm.* 27, 717.)

When dry chlorine gas in large excess is brought in contact with pulverized arsenic, terchloride of arsenic is formed at first, but at last there is produced a small quantity of a white crystalline substance, which may perhaps be *Pentachloride of Arsenic.* (Dumas.) According to Capitaine (*J. Pharm.* 5, 524), the small crystals thus formed consist of arsenious acid, proceeding from a small quantity of moisture in the chlorine, and are produced in but very small quantity if the chloride of calcium tube used to dry the chlorine is very long. When common salt is distilled with arseniate of potash and a large excess of oil of vitriol, a considerable quantity of chlorine is evolved and terchloride of arsenic is the only product. (Liebig & Wöhler, *Pogg.* 11, 49.) Similarly, if arsenic acid be used instead of arseniate of potash. (H. Rose, *Pogg.* 52, 64; Capitaine.) Rose likewise obtained nothing but terchloride of arsenic on treating metallic arsenic with excess of chlorine.

B. CHLORIDE OF SULPHUR AND ARSENIC.—Entire lumps of tersulphide of arsenic exposed to dry chlorine gas, deliquesce, with considerable development of heat, and are converted into a brown liquid, which refuses to take up more chlorine. This liquid dissolves completely in dilute nitric acid, giving off nitrous acid vapours, and forming a solution of sulphuric, hydrochloric, and arsenious acid. With water, it forms a solution containing hydrochloric, sulphuric, hyposulphurous, and arsenious acid, the hyposulphurous acid being however quickly resolved into sulphurous acid and precipitated sulphur. The solution of this compound in aqueous ammonia is rendered milky by sulphuric acid: it likewise contains hyposulphurous acid. (H. Rose, *Pogg.* 42, 536.)

			H. Rose.
As	75·0	22·36	
3S	48·0	14·31	13·68
6Cl	212·4	63·33	63·10
$AsCl^3 + 3SCl$	335·4	100·00	

Bisulphide of arsenic behaves in a similar manner, forming a yellowish liquid with a small quantity of chlorine, and a brown liquid with a larger quantity. (H. Rose.)

ARSENIC AND FLUORINE.

TERFLUORIDE OF ARSENIC.—Formed by mixing 1 part of ignited fluorspar with 1 part of arsenious acid and 3 parts of oil of vitriol in a leaden retort, and heating the mixture till it boils. Transparent, colourless, thin liquid, of specific gravity 2·73. Boils at 63°; fumes very strongly in the air even at ordinary temperatures; smells like fluoride of silicium, without any garlic odour; reddens litmus paper, if moisture has access to it, but not otherwise. (Unverdorben.) Fluoride of arsenic is very volatile. The specific gravity of the vapour is at least four times as great as that of air. A drop coming in contact with the skin—although it evaporates almost instantly, and in so doing produces a sensation of cold, like ether—nevertheless excites inflammation and protracted suppuration of the part, just like a burn; the vapour also produces a painful sensation under the nails, just as hydrofluoric acid does. (Dumas, *Ann. Chim. Phys.* 31, 434.)

	Calculation.		Unverdorben.
As	75·0	57·21	59·28
3F	56·1	42·79	40·72
AsF^3	131·1	100·00	100·00

Zinc, tin, and carbonate of lime are scarcely attacked by fluoride of arsenic; glass, for the most part, only when moisture is also present. The compound may therefore be kept for some time in glass vessels, in which it developes fluoride of silicium but slowly. It may be evaporated without decomposition in a glass vessel, to which the air has not excess; but if evaporated on glass in the open air, it is decomposed, the moisture of the air acting upon it in such a manner, that arsenious acid is left behind. It may be mixed—with more or less decomposition—with alcohol and ether, and somewhat less easily with oils, both fixed and volatile. It combines with ammonia. Mixes with water, forming a clear liquid which scarcely attacks zinc or tin, but when kept in glass vessels is decomposed, silica being dissolved and arsenious acid precipitated. (Unverdorben, *N. Tr.* 9, 1, 23; *Pogg.* 7, 316.)

ARSENIC AND NITROGEN.

A. ARSENITE OF AMMONIA.—*Volatile Liver of Arsenic, Arsenical Sal-ammoniac.*—Pulverized, transparent arsenious acid becomes heated in contact with aqueous ammonia. (Guibourt.) When aqueous ammonia is poured upon pulverized arsenious acid, an acid compound *b* is produced, in the form of a viscid crystalline deposit, and above it a liquid containing a basic compound *a*. (Fischer.)

a. Basic Salt.—The above-mentioned solution, when exposed to the air, gives off ammonia and deposits arsenious acid. (Fischer.) Arsenious acid dissolves abundantly in heated ammonia, but on cooling, is almost wholly deposited in octohedrons which do not contain ammonia. (Berzelius.) On evaporating the solution, Lassonne (*Crell. Chem. J.* 5, 80) likewise obtained a great number of small crystals [probably consisting merely of arsenious acid].

b. Acid Salt.—The viscid mass which settles at the bottom of the liquid. On warming the liquid and agitating it with the viscid mass till the latter is dissolved, the salt *b* crystallizes out in rhombic prisms. The salt *b*, when exposed to the air, is likewise converted into arsenious acid. It dissolves in water, and also, though less easily, in a large excess of ammonia. The aqueous solution gives very delicate reactions with copper and silver salts; a small quantity of alcohol precipitates arsenious acid from it; a large quantity leaves it transparent. (Fischer, *Kastn. Arch.* 11, 236.)

¶ According to Pasteur, the crystalline mass obtained by pouring strong ammonia on arsenious acid consists of NH^4O,AsO^3; the crystals are oblique rectangular prisms, having two of their lateral edges replaced by planes, so that they look like hexagonal tables. This salt remains permanent only when in contact with the ammoniacal solution; when taken out or dissolved in water, it soon loses its ammonia; the aqueous solution gives with nitrate of silver a yellow precipitate of $2AgO,AsO^3$, and the supernatant liquid exhibits an acid reaction. ¶

B. ARSENIATE OF AMMONIA.—*a. Trisarseniate.*—The concentrated solution of *b* mixed with ammonia, solidifies to a magma of the salt *a* which is less soluble; when exposed to the air, however, it quickly evolves ammonia, and is reconverted into *b*. (Mitscherlich.)

b. Diarseniate.—Formed by adding ammonia to a concentrated aqueous solution of arsenious acid, till a precipitate is produced, and warming the solution till the precipitate redissolves; the liquid, if left to itself for a while, yields beautiful crystals. Any crystals that may form immediately on cooling, consist of the salt *a*: these however are soon converted into *b* by exposure to the air. (Mitscherlich.) The crystalline system and form of diarseniate of ammonia agree precisely with those of diphosphate of ammonia. Therefore, *Fig.* 91, 93, 94, and 95; only with the following small angular differences; i' : *the axis* $= 113° 30\frac{1}{2}'$; $i : u = 105° 46'$; $i : f = 70° 54'$; $u : u' = 85° 54'$; f : *the axis* $= 137° 23\frac{1}{2}'$, &c. (Mitscherlich.) Colour, green like that of violet-juice. Gives off, when heated, ammonia, water, sublimed arsenic, and nitrogen gas. (Scheele.) Effloresces in the air, giving off half its ammonia (no water) and being converted into *c*. (Mitscherlich.)

	Crystallized.			Mitscherlich.
$2NH^3$	34	19·32	+Aq.	34·7
AsO^5	115	65·34		65·3
$3HO$	27	15·34		
$2NH^3,HO,AsO^5+2Aq$	176	100·00		100·0

c. Mono-arseniate.—Formed by supersaturating ammonia with solution of arsenious acid and evaporating. The salt which Macquer obtained by gently heating arsenious acid with nitrate of ammonia, is probably also a mono-arseniate. Large crystals, identical in form with monophosphate of ammonia. *Fig.* 23 and 30, with the same angles. (Mitscherlich.) Strongly acid reaction. When heated, it gives off water, arsenious acid, and nitrogen gas, but no ammonia. (Berzelius.) Deliquescent and very easily soluble in water.

	Crystallized.			Mitscherlich.
NH^3	17	10·69	+Aq.	27·78
AsO^5	115	72·33		72·22
$3HO$	27	16·98		
$NH^3,2HO,AsO^5+Aq.$	159	100·00		100·00

C. HYPOSULPHARSENITE OF AMMONIUM.—*Zweifach-Schwefelarsenammonium, Zweifachschwefelarsen-Hydrothionammoniak.*—A compound of bisulphide of arsenic with sulphide of ammonium. A concentrated solution of bibasic sulpharsenite of ammonium, kept for a long time in a stoppered bottle, deposits the hyposulpharsenite on the sides of the vessel in small, dark brown grains united into a crust. When distilled, it evolves [hydrosulphate of?] ammonia and leaves realgar. Absorbs ammoniacal gas and becomes lighter-coloured in consequence, but gives it off again when exposed to the air. (Berzelius.)

D. AMMONIO-TERSULPHIDE OF ARSENIC.—Finely divided tersulphide of arsenic slowly absorbs ammoniacal gas without alteration of external appearance (Berzelius), the absorption going on for three weeks before saturation is attained. (Bineau, *Ann. Chim. Phys.* 70, 264.) The compound quickly gives off its ammonia in the air. Water extracts from it a small quantity of arsenite of ammonia, together with sulpharsenite of ammonium. (Berzelius.)

E. SULPHARSENITE OF AMMONIUM.—*Dreifach-Schwefelarsenammonium, Dreifachschwefelarsen-Hydrothionammoniak.*—*a. Terbasic Salt.*—$3NH^4S,AsS^3$.—Prepared by mixing a solution of orpiment in excess of hydrosulphate of ammonia with alcohol, and washing the deposited crystals with alcohol. White, light, feathery crystals, which, on exposure to the air, turn yellow, give off hydrosulphate of ammonia, and leave a residue of orpiment with a trace of hydrosulphate of ammonia. (Berzelius.)

b. Bibasic Salt.—$2NH^4S,AsS^3$.—1. Formed by dissolving orpiment in hydrosulphate of ammonia. The same solution, but containing free ammonia is obtained: (2) by dissolving orpiment in pure ammonia or in heated carbonate of ammonia; or (3) by dissolving arsenious acid in bihydrosulphate of ammonia. The solution obtained by the first method leaves when spontaneously evaporated, a brown pulverulent mixture of pentasulphide and a lower sulphide of arsenic; that obtained by (2) leaves a reddish-yellow residue. Alcohol precipitates from the solution a white crystalline substance, which turns brown after a few seconds; if, however, it is mixed with bihydrosulphate of ammonia, a milky turbidity is first produced, and afterwards the compound *a* separates. (Berzelius.)

F. AMMONIO-PENTASULPHIDE OF ARSENIC.—Pentasulphide of arsenic absorbs ammoniacal gas, and is thereby converted into a pale yellow substance, which gives up all its ammonia when exposed to the air for a few hours, but is previously soluble in water: the solution gradually deposits a reddish-yellow powder.

G. SULPHARSENIATE OF AMMONIUM.—*Terbasic Salt.*—$3NH^4S,AsS^5$.—A solution of pentasulphide of arsenic in excess of bihydrosulphate of ammonia is gently heated and then mixed with hot alcohol and agitated. On cooling, the salt *a* separates in colourless prisms, which, after being washed with alcohol and dried by pressure, are tolerably permanent in the air, but generally turn yellow on the surface: when distilled, they melt, give off a small quantity of water, and afterwards a yellow liquid, containing sulphide of ammonium with excess of sulphur, and leave a residue of tersulphide of arsenic.

$$3NH^4S, AsS^5 = 3NH^4S + 2S + AsS^3.$$

b. Bibasic Salt.—$2NH^4S,AsS^5$.—Formed by dissolving pentasulphide of arsenic in ammonia. The solution, when left to evaporate spontaneously, dries up to a thick, glutinous, reddish-yellow mass, which cannot be perfectly dried without decomposing. Behaves like *a* when distilled, the liquid which passes over containing bisulphide of ammonium:

$$2NH^4S, AsS^5 = 2(NH^4S^2) + AsS^3.$$

c. Monobasic Salt.—NH^4S, AsS^5.—Remains in the alcoholic solution obtained in the preparation of *a*.

d. With 12 *atoms of acid.*—$NH^4S, 12AsS^5$.—The aqueous solution *a* or *b*, when boiled in a retort, evolves bihydrosulphate of ammonia, assumes a deep reddish yellow tint, and on cooling deposits this compound in the form of a yellow powder. (Berzelius.)

H. AMMONIO-CHLORIDE OF ARSENIC.—Chloride of arsenic absorbs ammoniacal gas at ordinary temperatures, evolving heat and forming a white powder. (Persoz, *Ann. Chim.* 44, 320; H. Rose, *Pogg.* 52, 62.)—The powder dissolves gradually in water, and may possibly be thereby converted into hydrochlorate and mono-arseniate of ammonia.

$$4NH^3, AsCl^3 + 3HO = 3(NH^3, HCl) + NH^3, AsO^3.$$

But the ammonia contained in the solution is in a peculiar state of combination, for it is but partially precipitated by bichloride of platinum. (H. Rose.)—The solution, saturated while hot, yields, on evaporation, white saline crusts, which, after careful washing, are found to contain ammonia, chlorine, and arsenic. If the whole powder be boiled with alcohol, the resulting solution deposits transparent cubes, which have the same composition as the powder, but are more readily soluble in water. Oil of vitriol withdraws the ammonia from the powder, and evolves the chloride of arsenic. (Liebig & Wöhler, *Ann. Pharm.* 11, 149.)

			H. Rose.	Persoz.
$4NH^3$	68·0	27·29	24·82	15·92
As	75·0	30·09	31·16	84·08
3Cl	106·2	42·62	44·02	
$4NH^3,AsCl^3$	249·2	100·00	100·00	100·00

¶ According to Pasteur (*J. Pharm. Chim.* 13, 395), the white substance produced by the action of ammonia on terchloride of arsenic, is composed of chlorimide of arsenic, chloride of ammonium, and ammonia: $2\,(ClAsNH) + 4\,(NH^4Cl) + NH^3$. When heated it first evolves ammonia, then sublimes undecomposed, and lastly yields a sublimate consisting chiefly of sal-ammoniac. Boiling water converts it into ammonia, arsenious acid, and sal-ammoniac. When treated with cold water, it becomes heated, and evolves ammonia; and the liquid, when evaporated, yields a precipitate consisting of small six-sided tables, containing 13·4 per cent. of chlorine, 58·1 arsenic, 5·3 nitrogen, and 2·3 hydrogen, corresponding to the formula: $ClAs^2NH^5O^7$. The formation of this compound is expressed by the following equation:—

$$2(ClAsNH) + 7HO = ClAs^2NH^5O^7 + NH^4Cl.$$

When treated with strong ammonia, it is converted into neutral arsenite of ammonia NH^4O,AsO^2. ¶

I. Ammonio-fluoride of Arsenic.—Fluoride of arsenic rapidly condenses ammoniacal gas, producing white fumes, and rapidly separates carbonic acid from carbonate of ammonia. In both cases, a white friable mass is formed, which sublimes without decomposition. It dissolves without decomposition in a small quantity of boiling water, and partially crystallizes out again as the liquid cools. When a solution of this compound in a large quantity of water is evaporated in a glass vessel, the glass is attacked, and part of the compound decomposes, while the rest volatilizes unaltered. (Unverdorben, *N. Fr.* 9, 1, 24.)

			Unverdorben.
$3NH^3$	51·0	28·01	27·54
AsF^3	131·1	71·99	72·46
$3NH^3,AsF^3$	182·1	100·00	100·00

Arsenic and Potassium.

A. Arsenide of Potassium.—1. Three volumes of arsenic powder easily unite with one volume of potassium, the combination being attended with vivid combustion. (Gay-Lussac & Thénard; H. Davy.)—Potassium heated in arseniuretted hydrogen gas, takes the arsenic to itself, and sets free twice as much hydrogen gas as it would have evolved from water. (Gay-Lussac & Thénard.) Hence the compound formed is K^3As.—3. When arsenic conveys the negative electricity of a voltaic circuit into hydrate of potash, it forms a dark grey metallic alloy, which, when immersed in water, evolves arseniuretted hydrogen gas, and deposits brown, pulverulent arsenide of hydrogen. (H. Davy, *vid.* p. 264.)—Chestnut-brown without metallic lustre.—With water it evolves a quantity of arseniuretted hydrogen gas, the volume of which is equal to half the volume of hydrogen which the potassium contained in it would have evolved; solid arsenide of hydrogen is formed at the same time. (Gay-Lussac & Thénard.)—If 100 parts (3 At.) of potassium are fused by continued ignition with 64 parts (1 At.) of arsenic in a glass tube, drawn out to a narrow neck, and the mass treated with water, a quantity of hydrogen, equal to $\frac{1}{8}$ of that which the pure potassium would have separated from water, is evolved in the free state [probably because some of the potassium has not combined with the arsenic]; $\frac{6}{8}$ goes off in the form of arseniuretted hydrogen gas, and $\frac{1}{8}$ remains combined with the arsenic in the form of solid arsenide of hydrogen. (Soubeiran, *J. Pharm.* 16, 353.) —On heating 1 part of arsenic with 3 parts of potash in solution, then evaporating to dryness, and heating the residue to commencing redness, hydrogen gas is evolved, and there remains a dark brown, tumefied mass [containing arsenide of potassium], which, when put into water, becomes heated, and gives off arseniuretted hydrogen. (Gehlen.)

B. ARSENITE OF POTASH.—*Fixed Liver of Arsenic.*—Arsenious acid dissolves easily in aqueous solution of potash; from a solution of carbonate of potash it does not expel the carbonic acid until heat is applied, and even then but slowly.—Potash-ley saturated while hot with arsenious acid, deposits a small quantity of that substance on cooling; the yellowish, strongly alkaline mother-liquid leaves a gummy residue on evaporation. This residue, when more strongly heated, swells up considerably, gives off a small quantity of water, fuses tranquilly, and, if more strongly ignited, evolves a small quantity of arsenious acid. The cooled mass has the appearance of enamel, and dissolves very slowly in water; even when hot, a small portion of the arsenite of potash is found to be converted into arseniate. (Simon, *Pogg.* 40, 442.)

¶ *a. Di-arsenite.*—$2KO,AsO^3$. Formed by digesting the acid salt *c* with excess of potash, and precipitating with alcohol. Gives with nitrate of silver a yellow precipitate, consisting of $2AgO,AsO^3$; the supernatant liquid becomes neutral. (Pasteur.)

b. Mono-arsenite.—KO,AsO^3.—Formed by boiling *c* for several hours with carbonate of potash, whereupon carbonic acid is evolved, and there remains a salt which is but slightly soluble in alcohol, and after repeated washing with alcohol, is obtained in the form of a syrupy mass: this is the mono-arsenite. (Pasteur.) Filhol did not succeed in obtaining this salt in a state of purity.

c. Bi-arsenite.—$KO,HO,2AsO^3 + Aq$.—When arsenious acid in excess is digested in cold solution of potash, an oily alkaline liquid is obtained, which does not crystallize, but, when mixed with the solution of a silver-salt, gives a yellow precipitate of neutral arsenite of silver, mixed with free arsenious acid, while the supernatant liquid acquires an acid reaction; hence it follows, that the solution must contain an acid salt. This compound is obtained by mixing the oily solution with alcohol, whereupon it becomes thick and turbid, and after a few days deposits on the sides of the vessel, beautiful crystals, having the form of right rectangular prisms and the composition above stated. At 100°, they give off one atom of water. (Pasteur.) ¶

C. ARSENIATE OF POTASH.—*a. Tris-arseniate.*—$3KO,AsO^5$.—One atom of diarseniate of potash ignited with excess of carbonate, liberates one atom of carbonic acid. (Mitscherlich.) Aqueous arsenic acid supersaturated with potash, crystallizes almost wholly, on evaporation, in small, very deliquescent needles. (Graham, *Pogg.* 32, 47.)

b. Di-arseniate.—$2KO,AsO^5$.—Formed by adding carbonate of potash to aqueous arsenic acid, as long as effervescence continues. Colours violet-juice green; does not crystallize; fuses to a white glass when heated; deliquesces in the air. (Scheele.)

c. Mono-arseniate.—KO, AsO^5.—*Macquer's arsenikalisches Mittelsalz.*—1. Formed by deflagrating equal parts of arsenious acid and nitre, dissolving the mass in water, and leaving the solution to crystallize. (Macquer, Glaser, *Mag. Pharm.* 15, 132.)—2. By mixing aqueous carbonate of potash with such a quantity of arsenic acid, that the solution may redden litmus paper, but the redness may disappear as the paper dries—and then evaporating. (Mitscherlich.) On evaporating a mixture of potash-ley and arsenic acid, neutral to vegetable colours, the simple salt crystallizes out, while an alkaline bibasic salt remains in solution. Mono-arseniate of potash crystallizes in the same forms and with exactly the same angles as the monophosphates of potash and ammonia, and mono-arseniate of ammonia, *Fig.* 23 and 30. (Mitscherlich.) More solid than the corresponding soda-salt: of specific gravity 2·63·8; tastes like nitre. (Thomson, *Ann. Phil.* 15, 85.) The redness imparted to litmus-paper by the solution of this salt disappears on drying. (Mitscherlich.)

	Anhydrous.		Mitscherlich.
KO	47·2	29·1	29·2
AsO^5	115·0	70·9	70·6
KO,AsO^5	162·2	100·0	99·8

	Crystallized.		Thomson.	Mitscherlich.
KO	47·2	26·19	27·07	89·91
AsO^5	115·0	63·82	65·43	
$2HO$	18·0	9·99	7·50	10·09
$KO,2HO,AsO^5$	180·2	100·00	100·00	100·00

The crystals are permanent in the air, and give off but little water even at 288°. At a red heat, they fuse, give off water, and are converted into a pale yellow, very thin liquid, which, on solidifying, becomes white and opaque and splits in all directions. (Thomson.) The crystals dissolve in 5·3 parts of water at 6°, forming a solution of specific gravity 1·1134; they dissolve in a much smaller quantity of hot water, but not in alcohol. (Thomson.) The aqueous solution does not precipitate the salts of the earthy alkalis or of the earths. (Mitscherlich.)

D. HYPOSULPHARSENITE OF POTASSIUM.—*Terbasic Salt.*—$3KS,AsS^3$. Orpiment is boiled in a moderately concentrated solution of carbonate of potash; the liquid filtered boiling hot; and the brownish red flakes of *b*, which separate from the colourless filtrate, are first washed on a filter, with a small quantity of cold water, till they swell up like a jelly and begin to dissolve—then treated with a larger quantity of water—and the dark-red filtrate thus obtained, is evaporated to dryness. (That which remains on the filter is the compound *c.*)—Red translucent mass. Forms with water a yellowish-red solution—deep red in large quantity—which, when evaporated, becomes gelatinous before it dries up. This effect is probably due to the presence of sulpharseniate of potassium, which displaces the hyposulpharsenite in the water.

b. Bibasic Salt.—$2KS, AsS^3$.—The brown-red flakes which separate during the preparation of *a*.

c. Monobasic Salt.—KS, AsS^3.—The substance left on the filter in the preparation of *a*.—Dark brown powder, insoluble in water, which easily fuses when heated, without giving anything off, and afterwards on cooling, solidifies to a dark red, translucent mass. It dissolves in potash with the same appearances as realgar. (Berzelius.)

E. SULPHARSENITE OF POTASSIUM.—*a. Terbasic Salt.*—$3KS,AsS^3$.—Precipitated on mixing the aqueous solution of *b* with alcohol, in the form of a syrup, which is colourless at first, but soon becomes dark brown and deposits $\frac{1}{6}$-sulphide of arsenic.

b. Bibasic Salt. $2KS, As^3$.—Formed by heating sulpharseniate of potassium in a retort till the excess of sulphur is evolved. Dark coloured while fused, yellow after cooling. When treated with a small quantity of water, it is resolved into hyposulpharsenite of potassium which is precipitated, and sulpharseniate which remains in solution.

c. Monobasic Salt.—KS, AsS^3.—Formed by saturating mono- or bihydrosulphate of potash in the cold with orpiment.—Likewise obtained, mixed with arsenite of potash, when orpiment is dissolved in caustic potash or its carbonate, or when arsenious acid is dissolved in bihydrosulphate of potash (p. 275).—The solution, even when evaporated at ordinary temperatures, becomes turbid, and deposits a brown powder, consisting of hyposulpharsenite of potassium. When a solution saturated with orpiment at ordinary temperatures, is heated with a larger quantity of orpiment prepared in the moist way, the orpiment is converted into realgar, and sulpharseniate of potassium is produced.

d. With excess of acid.—Formed when carbonate of potash is heated in a retort with excess of orpiment till the portion of the latter which is least strongly retained, is driven off. From this compound, water extracts the compound *c*, and leaves a red compound, containing a still larger excess of orpiment and soluble in ammonia, together with hyposulpharsenite of potassium which is insoluble in ammonia. (Berzelius.)

F. SULPHARSENIATE OF POTASSIUM.—*a. Terbasic.*—$3KS, AsS^5$.—The aqueous solution of *b*, when mixed with alcohol, becomes milky, and deposits a concentrated solution of *a*, in the form of an oily liquid, which, when dried at a gentle heat, leaves a fibrous, deliquescent mass.

b. Bibasic Salt.—$2KS, AsS^5$.—Formed by saturating aqueous diarseniate of potash with hydrosulphuric acid, and evaporating the liquid in vacuo.—The residue is a viscid, yellowish, somewhat crystalline mass, which does not dry up completely, but, when exposed to the air, first liquefies, and then solidifies in a crystalline mass containing rhombic tables.

c. Monobasic Salt.—KS, AsS^5.—On mixing the solution of *b* with alcohol, *a* is precipitated and *c* remains in solution. The solution is decomposed on evaporation, and deposits crystals of octodecasulphide of arsenic.—2. Aqueous hydrosulphate of potash dissolves, at ordinary temperatures, more than $\frac{1}{2}$ At. but less than 1 At. of pentasulphide of arsenic. The solution, when evaporated in the air, first becomes covered with a film of sulphur, then deposits a red crust, and by this loss of sulphide of arsenic, is converted into the bibasic compound *b*, which dries up first to a stiff syrup and then to a lemon-yellow mass. (Berzelius.)

d. With 12 *atoms of acid.*—$KS,12AsS^5$.—Precipitated when the solution of *b* is decomposed by carbonic acid; similarly on passing hydrosulphuric acid gas through mono-arseniate of potash.—Yellow powder, containing 2·9 sulphide of potassium to 97·1 pentasulphide of arsenic. (Berzelius.)

¶ G. SULPHOXIARSENIATE OF POTASH. KO, AsO^3S^2+HO. For the preparation of this salt, see page 280. Crystallizes in small, white, elongated prisms, sometimes 1 or 2 centimetres in length; slightly soluble in water. The dry salt is permanent in the air; gives up all its water at 170°, without melting. Fuses over the spirit-lamp, giving off first arsenic sulphide and then metallic arsenic.

	Crystallized.		Bouquet & Cloez.
As	75·0	38·26	38·02
2S	32·0	16·37	16·10
3O	24·0	12·21	12·43
KO	47·2	24·01	23·69
2HO	18·0	9·15	9·50
$KO,AsO^3S^2+2Aq.$	196·2	100·00	99·74

The aqueous solution decomposes rapidly at a boiling heat, giving off hydrosulphuric acid and depositing sulphur. If hydrochloric acid be then added, a precipitate of sulphide of arsenic is obtained. From the salt itself, hydrochloric acid precipitates nothing but sulphur, and the precipitation is complete; the filtrate then contains arsenious acid. Lead-salts added to the solution give a white precipitate, which soon turns black. (Bouquet & Cloez, *N. Ann. Chim. Phys.* 13, 44; abstr. *Ann. Pharm.* 56, 216.) ¶.

H. ARSENITE OF IODIDE OF POTASSIUM.—Precipitated on mixing the aqueous solutions of iodide of potassium and arsenious acid, or of iodide of potassium and arsenite of potash. In the former case, the arsenious acid is completely precipitated; in the latter, part of it remains dissolved in combination with excess of potash. If arsenite of potash (obtained by boiling arsenious acid with aqueous solution of caustic potash and leaving the solution to cool) be mixed with such a quantity of acetic acid, that the solution shall no longer redden turmeric paper—and iodide of potassium be then added—a quantity of arsenious acid is precipitated sufficient to restore the alkaline reaction. After washing with cold water and drying, the compound is obtained in the form of a white powder:

	Calculation.		Emmet.
KI	165·2	35·77	36·7
$3AsO^3$	297·0	64·23	63·3
$KI,3AsO^3$	462·2	100·00	100·0

The compound is decomposed at 315°, evolving large quantities of arsenic vapour, and afterwards at a higher temperature, giving off iodine: the loss amounts to 31 per cent. The residue, when treated with oil of vitriol, acquires a deep brown tint, from separation of iodine and iodide of arsenic. The unignited compound acquires a black-brown tint by contact with strong nitric acid and heated oil of vitriol, and bright yellow with cold oil of vitriol. It dissolves in 19 parts of boiling water. (Emmet, *Sill. Amer. J.* 18, 58.)

ARSENIC AND SODIUM.

A. ARSENIDE OF SODIUM.—*a.* Three volumes of arsenic powder unite below a red heat with one volume of sodium, emitting a faint light and forming a brittle, fine-grained mass, which oxidates quickly in the air, and when thrown into water produces arseniuretted hydrogen gas and solid arsenide of hydrogen.—*b.* One volume of arsenic produces with 2 volumes of sodium an earthy chestnut-brown compound, without metallic lustre, which exhibits the same reactions. The same brown compound is likewise formed by heating sodium in arseniuretted hydrogen gas. (Gay-Lussac & Thénard.)

B. Arsenite of Soda.—Viscid, yellow, foul-smelling liquid, from which, when concentrated to the consistence of a syrup, provided it contains excess of soda, small grains are deposited. ¶ According to Pasteur, arsenious acid forms with soda three salts, exactly corresponding in composition to the arsenites of potash (p. 291); but the acid salt, $NaO,2AsO^3$, refuses to crystallize. ¶

C. Arseniate of Soda.—*Tris-arseniate.*—One atom of di-arseniate of soda ignited with excess of carbonate of soda, drives out one atom of carbonic acid. (Mitscherlich.)—If to a concentrated solution of the bibasic salt *b*, there be added at least half as much carbonate as it already contains (the liquid should feel soapy), and the solution be then evaporated to dryness, the hydrated salt separates almost completely, while the mother-liquid retains scarcely anything but the excess of soda. The crystals are purified by rapid drying between blotting-paper, solution in twice their weight of hot water, and crystallization.—Right rhombic prisms, truncated at the acute lateral edges (*fig.* 70°). Taste strongly alkaline. In the dry state, they are permanent in the air; they fuse at 85·5°. (Graham.)

	At.		*Anhydrous.*			At.	*Crystallized.*				Graham.
NaO	3	....	93·6	....	44·87	3	93·6	....	22·04	....	22·85
AsO^5...........	1	....	115·0	....	55·13	1	115·0	....	27·09	....	27·76
HO		....		....		24	216·0	....	50·87	....	50·22
$3NaO,AsO^5$	1	....	208·6	....	100·00	+24Aq.	424·6	....	100·00	....	100·83

The crystals, when ignited alone in a platinum flask, lose 49·75 per cent. of water; and if afterwards ignited with arsenious acid, mono-arseniate of soda, or bichromate of potash, they give off 0·47 per cent. more. Also, when the ignited salt is finely pounded, and then again ignited, it gives off nearly all its water. The ignited residue does not fuse, even at a white heat; it attacks glass like caustic soda. When it is ignited in the air, the residue greedily absorbs carbonic acid, whereby the 0·47 per cent. of residual water is expelled. In a similar manner, this residual water is expelled by ignition with carbonate of ammonia, the 0·47 per cent. of water being replaced by 1·055 per cent. of carbonic acid, and the hydrate of soda, which may be supposed to exist in the ignited residue, being thereby converted into carbonate. The carbonic acid thus absorbed is not expelled, even at a white heat. [This retention of 0·47 per cent. of water might be easily explained, by supposing that the salt contained more than 3 atoms of soda to 1 atom of acid, and that the excess of soda was present in the form of hydrate; Graham, however, maintains that the salt which he used was so pure, as to render such a mode of explanation inadmissible.]—The aqueous solution of the salt attracts carbonic acid from the air, and is thereby converted into diarseniate of soda. A similar action is produced by other weak acids, also by chlorine and iodine, and by nitrate of ammonia, from which ammonia is given off.—The salt dissolves in 3·57 parts of water at 15°·5 (Graham, *Pogg.* 32, 33.)

b. Di-arseniate.—Formed by adding carbonate of soda to aqueous arsenic acid, till the liquid acquires a strong alkaline reaction, then evaporating, and leaving the solution to crystallize. The crystals when ignited leave the anhydrous salt, which is a white mass, having an alkaline reaction, and easily fusing to a transparent and colourless liquid. The salt remains liquid for a long time after fusion, but ultimately solidifies in a fibrous mass, having a silky lustre. (Marx.) When ignited in a current of hydrogen gas, it evolves arsenic and is converted into hydrate of soda. (Soubeiran.) No modification analogous to pyrophosphate of soda can be obtained by ignition. (Clark.)

	Ignited.			Mitscherlich.
$2NaO$	62·4	....	35·18	34·16
AsO^5	115·0	....	64·82	65·84
$2NaO,AsO^5$	177·4		100·00	100·00

On crystallizing from the aqueous solution, the salt takes up 15 atoms of water into its crystals, if the solution be warm and concentrated, and 25 atoms if it be cold and dilute.

α. With 15 atoms of water.—$2NaO,HO,AsO^5+14Aq$.—Crystalline system the oblique prismatic. *Fig.* 108, with the *f*-face; $i : t=97°$; $i : a=123° 22'$: $i : f$, *behind*$=128° 27'$; $i : u=94° 26'$; $i : h$, *behind* $= 116° 42'$; $u : u' = 78° 46'$; $z : z = 117° 16'$; $t : f = 134° 33'$.—Cleavage parallel to t'. (Haidinger, *Edinb. J. of Sc.* 7, 314; *compare* Marx, *Kastn. Arch.* 2, 18; Bernhardi, *N. Tr.* 11, 1, 10; L. Gmelin, *Pogg.* 4, 157.)—The crystals do not effloresce even in warm air. At a heat below redness they give off 41·18 per cent. (14 At.) of water; afterwards, at a red heat, 2·96 per cent. (1 At.), and leave 55·86 per cent. of anhydrous salt. (Clark, *Edinb. J. of Sc.* 7, 309; also *Schw.* 57, 437, and 440; abstr. *Pogg.* 16, 609.)

β. With 25 atoms of water.—$2NaO,HO,AsO^5+24Aq$.—Crystalline form exactly like that of diphosphate of soda with 25 At. water, described at page 92, Vol. III. (Mitscherlich); *Fig.* 96, 97, 98, 99, 100. The crystals effloresce very quickly in the air, even at 9°, and are converted into the salt *α*. (Clark.)—They dissolve very readily in water.

	At.		*Salt α.*		Clark.	Gmelin.
NaO	2	62·4	....	19·98	55·86	56
AsO^5	1	115·0	....	36·81		
HO	15	135·0	....	43·21	44·14	44
	1	312·4	....	100·00	100·00	100

	At.		*Salt β.*		Mitscherlich.
NaO	2	62·4	....	15·51	44·19
AsO^5	1	115·0	....	28·58	
HO	25	225·0	....	55·91	55·81
	1	402·4	....	100·00	100·00

c. Mono-arseniate.—Formed by adding arsenic acid to an aqueous solution of carbonate of soda, till the liquid no longer precipitates chloride of barium, then evaporating, and leaving the concentrated solution for some time in a cold place.—Large crystals, precisely similar in form and in the magnitude of their angles, to those of phosphate of soda when that salt is crystallized by method 2, page 93, Vol. III. (*Fig.* 94). More soluble in water than *b*. (Mitscherlich.)—From a solution of soda and arsenic acid, mixed in such proportions as to be neutral to vegetable colours, di-arseniate of soda crystallizes first, and then the liquid shows an acid reaction. If to an aqueous solution of 3 atoms of di-arseniate of soda, there be added 2 atoms of sulphuric acid, the liquid immediately begins to redden litmus, but still colours turmeric brown. (Mitscherlich.) The result is a mixture of 4 atoms of soda and 3 atoms arsenic acid.

$$3(2NaO, AsO^5) + 2SO^3 = 2(NaO, SO^3) + 4NaO, 3AsO^5.$$

This salt is not converted by ignition into a modification analogous to metaphosphate of soda. (Graham.)

		Ignited.	Mitscherlich.			*Crystallized.*	Mitscherlich.
NaO	31·2	21·34	21·68	NaO	31·2	17·12	17·36
AsO^5	115·0	78·66	78·32	AsO^5	115·0	63·12	62·70
				$4HO$	36·0	19·76	19·94
NaO, AsO^5	146·2	100·00	100·00	$+4Aq.$	182·2	100·00	100·00

D. Hyposulpharsenite of Sodium.—The terbasic, bibasic, and monobasic salts are precisely similar to the corresponding potassium compounds. (Berzelius.)

E. Sulpharsenite of Sodium.—Analogous to the potassium compound. (Berzelius.)

F. Sulpharseniate of Sodium.—*a. Terbasic Salt.*—$3NaS, AsS^5$.—*α. Anhydrous.*—The compound *β* heated without access of air, fuses quietly after having parted with its water, and forms, without decomposition, an oily liquid, which on cooling yields a solid yellow mass. This substance, when immersed in water, is first converted into the crystalline compound *β*, and then dissolves.

β. Hydrated, crystallized.—1. Prepared by precipitating a solution of *b* with alcohol.—2. By leaving a mixture of *b* and bi-hydrosulphate of soda to spontaneous evaporation.—3. By digesting the alcoholic solution of pentasulphide of sodium with orpiment, pouring the liquid off, washing the residue with alcohol, then dissolving out the terbasic salt with water, and leaving the solution to crystallize.—4. By dissolving pentasulphide of arsenic in aqueous solution of soda, and leaving the liquid to crystallize. The crystals obtained by either of these methods are washed on a filter with alcohol, then pressed out and dried. (Berzelius.)—5. By boiling 1 part of sulphur, 1½ of orpiment, and 8 of crystallized carbonate of soda with water, and purifying the crystals obtained from the filtrate by recrystallization. (Rammelsberg, *Pogg.* 52, 238.)—By method (1): snow-white crystals; by (4): ill-defined rhomboidal tables. Crystallizes by slow cooling from a hot aqueous solution in irregular six-sided prisms, with two of their lateral edges more acute than the rest. By spontaneous evaporation or very slow cooling, it crystallizes in transparent rhombic prisms with dihedral summits resting on the acuter lateral edges; and by still slower cooling, till the temperature falls below 0°, in white, opaque, rhombic octohedrons. (Berzelius.)—Oblique rhombic prisms, *fig.* 85, together with *m*-faces; $u' : u = 113° 40'$; $i : m$ (or : the axis) $= 120°$; $f : m = 103° 20'$. (Rammelsberg.)—The opaque crystals are milk-white; the transparent crystals are yellowish, and have somewhat of a diamond lustre. (Berzelius.)

Crystallized.			Or:			Berzelius.	Rammelsberg.
3Na	69·6	17·08	3NaS	117·6	28·85	28·47	28·52
As	75·0	18·40	AsS^5	155·0	38·03	38·03	37·32
8S	128·0	31·40	15HO	135·0	33·12	33·50	34·16
15HO	135·0	33·12					
	407·6	100·00		407·6	100·00	100·00	100·00

In the dry state, it is permanent in the air; even in vacuo over oil of vitriol, it does not give up its water till gently heated; it then becomes milk-white; when more strongly heated, it gives off a small quantity of hydrosulphuric acid, and turns yellow. Heated in a retort, it fuses in its water of crystallization, forming a very pale yellow liquid,—then gives off water, and is converted into a white salt, which, when more strongly heated, decrepitates slightly, evolves the remaining water and a small quantity of hydrosulphuric acid, and fuses to a dark red liquid; on cooling, this liquid solidifies and forms the yellow anhydrous compound *α.* (Berzelius.)—Decomposed completely by boiling with sulphate of copper, yielding a precipitate of sulphide of copper, while soda, sulphuric acid, and arsenic acid remain in solution.

$$3NaS, AsS^5 + 8(CuO, SO^3) = 8CuS + 3NaO + AsO^5 + 8SO^3.$$

A similar decomposition takes place with acetate of lead; but the precipitated sulphide of lead [if the acetate is in excess], is mixed with arseniate of lead, because that salt is insoluble in acetic acid. (Rammelsberg.)—The salt dissolves easily and abundantly in water. (Berzelius.)

b. Di-acid Salt.—$2NaS, AsS^5$.—The aqueous solution of di-arseniate of soda, saturated with hydrosulphuric acid gas, and then left to evaporate spontaneously, yields a viscid liquid, and afterwards, if gently heated, a dry lemon-yellow mass. This substance fuses at a moderate heat, forming a very pale yellow liquid (losing water at the same time if warmed in an open vessel), and on cooling, solidifies in a yellow mass, which softens when exposed to the air. (Berzelius.)

c. Monobasic Salt.—NaS,AsS^5.—When the hydrated compound *α, β*, is prepared with alcohol according to method (1), the supernatant alcoholic solution contains the monobasic salt. On distilling off the alcohol, the liquid often deposits octodeca-sulphide of arsenic in beautiful crystals.

d. With 12 *atoms of acid.*—$NaS,12AsS^5$.—Obtained like the potassium compound. Yellow powder. (Berzelius.)

G. Arseniate of Soda and Ammonia.—An aqueous solution of equal parts of di-arseniate of soda and di-arseniate of ammonia yields crystals, whose form exactly agrees with that of phosphate of soda and ammonia (III., 118. *Fig.* 101, 102); these crystals, when heated to redness, yield mono-arseniate of soda.

	Crystallized.			Mitscherlich.
NH^3	17·0	6·71	+HO	43·04
NaO	31·2	12·32		56·06
AsO^5	115·0	45·42		
10HO	90·0	35·55		
$NH^4O,NaO,HO,AsO^5 + 8Aq.$	253·2	100·00		100·00

H. Sulpharseniate of Sodium and Ammonium.—*Terbasic.*—$(3NH^4S,AsS^5) + (3NaS,AsS^5)$.—1. Formed by adding warm alcohol to a mixture of the aqueous solutions of disulpharseniate of ammonium and disulpharseniate of sodium, and agitating the mixture. As the liquid cools, small four-sided tables crystallize out.—2. When a solution of trisulpharseniate of sodium in a small quantity of cold water is mixed with sal-ammoniac, and the liquid abandoned to spontaneous evaporation, the double salt crystallize out in six-sided prisms, perpendicularly truncated, and having two of their lateral faces broader than the rest.—The crystals are transparent, and either colourless or pale-yellow: they are permanent in the air. When distilled, they give off hydrosulphate of ammonia with a small quantity of water, and leave sulpharseniate of sodium. The double salt dissolves in water much more readily than the sodium salt alone. (Berzelius.) The aqueous mixture of disulpharseniate of ammonium and disulpharseniate of sodium, when evaporated without the addition of alcohol, leaves a dry yellow mass, having none of the characters of a double salt. (Berzelius.)

I. Arseniate of Soda and Potash.—Formed by neutralizing the aqueous solution of mono-arseniate of potash with carbonate of soda. The crystals exactly resemble those of the phosphate of soda and potash. (Mitscherlich, III. 119.) *Fig.* 107, 108. [Since these crystals appear to be isomorphous with those of diarseniate of soda with 15 atoms of water (p. 296), a question arises as to whether the crystals of the double phosphate and double arseniate of soda and potash do not also contain merely 15 atoms of water instead of 17. The formula is then the same; *viz.* KO,NaO,HO,AsO^5+14Aq, excepting that 1At. NaO is replaced by 1At. KO.]

Anhydrous.			*Crystallized.*			Mitscherlich.
KO........	47·2	24·41	KO	47·2	13·63	.... 56·12
NaO	31·2	16·13	NaO	31·2	9·01	
AsO^5	115·0	59·46	AsO^5	115·0	33·20	
			17Aq.	153·0	44·16	.... 43·88
	193·4	100·00		346·4	100·00	.... 100·00

K. Sulpharseniate of Sodium and Potassium.—*Terbasic Salt.*—Formed by mixing the aqueous solutions of the sulpharseniates of sodium and potassium, and crystallizing. Transparent and colourless, or pale yellow, four-sided tables. (Berzelius.)

Arsenic and Lithium.

A. Sulpharsenite of Lithium. Behaves like the corresponding compounds of potassium and sodium. (Berzelius.)

B. Sulpharseniate of Lithium.—*a. Terbasic Salt.*—Precipitated from the aqueous solution *b*, by the addition of alcohol, in large, colourless, shining, crystalline scales. When this precipitate is dissolved in hot water and the solution quickly cooled, the salt separates in six-sided prisms; by spontaneous evaporation, on the contrary, rhombic prisms are formed. These crystals are easily soluble in water; they behave like the corresponding sodium compound both during and after ignition, and must therefore contain water.

b. Bibasic.—The aqueous solution yields by evaporation a non-crystalline, lemon-yellow mass, which does not become moist in the air, and redissolves perfectly in water.

c. Monobasic.—*d. With* 12 *atoms of acid.*—Both these salts behave like the corresponding sodium compounds.

ARSENIC AND BARIUM.

A. ARSENITE OF BARYTA.—Aqueous arsenious acid when largely diluted, does not precipitate baryta-water in any proportion; when the liquid is somewhat more concentrated and the baryta more in excess, a precipitate is formed after a while; and when the strength of the solution and the excess of baryta are still greater, precipitation takes place immediately. (Gm.) Arsenite of ammonia gives a precipitate with chloride of barium, but not till after some time. (H. Rose.)

¶ *a. Di-arsenite.*—$2BaO,AsO^3$.—Formed by precipitating chloride of barium with di-arsenite of potash. Resembles *b* in external characters. Slightly soluble in water. (Filhol.)

b. Mono-arsenite.—BaO,AsO^3.—Precipitated, on mixing chloride of barium with mono-arsenite of potash or soda, in the form of a gelatinous magma, or in dendritic ramifications, which however show no sign of regular crystallization. The gelatinous mass is easily soluble in water, but after drying forms a white insoluble powder. On filtering the liquid from the gelatinous precipitate and boiling it, a heavy white powder having the same composition is precipitated. (Filhol.) ¶

B. ARSENIATE OF BARYTA.—*Tris-arseniate.*—By digesting *b* with aqueous ammonia. (Berzelius.)—2. By precipitating arsenious acid with excess of baryta-water. (Laugier).—3. By gradually dropping tris-arseniate of soda into chloride of barium—whereby a heavy powder is quickly formed—and rapidly washing the precipitate, so that it may not absorb moisture from the air. If, on the other hand, chloride of barium in solution be gradually added to an excess of tris-arseniate of soda, a gelatinous precipitate is obtained, which becomes finely flocculent on boiling: but the liquid is strongly alkaline, a proof that di-arseniate of baryta has been thrown down together with the tris-arseniate. The precipitate likewise carries with it a small quantity of tris-arseniate of soda, which cannot be completely extracted by washing. (Graham, *Pogg.* 32, 48.) Tris-arseniate of baryta is a white powder which attracts a small quantity of carbonic acid from the air. About 0·8 per cent. of carbonate of baryta may be formed by igniting the tris-arseniate in the air. (Graham.) Dissolves readily in cold hydrochloric, nitric, tartaric, and acetic acid (Anthon); very slightly soluble in water, somewhat more soluble in aqueous ammonia (Berzelius); its solubility in water does not seem to be increased by the presence of ammonia, potash, or soda salts. (Laugier.)

	Ignited.		Laugier.	Berzelius.	Graham.
$3BaO$	229·8	66·65	65·7	66·56	67·94
AsO^5	115·0	33·35	34·3	33·44	32·06
$3BaO,AsO^5$	344·8	100·00	100·0	100·00	100·00

b. Di-arseniate.—When di-arseniate of soda is mixed with excess of chloride of barium, this salt is precipitated, after a few seconds, in small, white, crystalline scales. (Berzelius.) The quantity of arseniate of soda must be less than sufficient to decompose the whole of the chloride of barium, and it must be added drop by drop; the first portions of precipitate disappear again [is then arseniate of baryta soluble to a certain extent in chloride of barium?] If, on the contrary, chloride of barium be gradually added to di-arseniate of soda, a precipitate is formed consisting of di-arseniate and tris-arseniate of baryta together, while mono-arseniate of baryta remains in solution. (Berzelius, Mitscherlich.) According to Scheele, free arsenic acid does not precipitate hydrochlorate, nitrate, or acetate of baryta. According to the author's experiments, it precipitates the acetate if not the other salts; according to Maretti, it gives a precipitate even with acid sulphate of baryta [due to the presence of water], and arseniate of baryta is not decomposed by sulphuric acid; the author, however, found that it is decomposed by digestion with dilute sulphuric acid. When ignited, it merely gives up its water of crystallization. By contact with water, it is resolved into the salt *c* which dissolves, and the salt *a* which remains behind. (Berzelius.)

	Ignited.		Berzelius.
$2BaO$	153·2	57·12	57·06
AsO^5	115·0	42·88	42·94
$2BaO,AsO^5$	268·2	100·00	100·00

	Crystallized.		Berzelius.
$2BaO$	153·2	50·36	50·32
AsO^5	115·0	37·80	37·86
$4HO$	36·0	11·84	11·82
$+4Aq.$	304·2	100·00	100·00

c. Mono-arseniate.—1. Formed by adding baryta-water to aqueous arsenic acid, as long as a precipitate continues to form.—2. By dissolving *b* in aqueous arsenic acid and leaving the solution to crystallize. Mono-arseniate of soda does not precipitate chloride of barium, but on adding the smallest quantity of ammonia, a precipitate is formed. The crystals contain water of crystallization, and are soluble in water.

	Ignited.		Mitscherlich.
BaO	76·6	39·98	40·13
AsO^5	115·0	60·02	59·87
BaO,AsO^5	191·6	100·00	100·00

C. HYPOSULPHARSENITE OF BARIUM.—Precipitated when an aqueous solution of the terbasic potassium-salt D (p. 292) is mixed with chloride of barium. Red-brown powder, insoluble in water. (Berzelius.)

D. SULPHARSENITE OF BARIUM.—*a. Terbasic Salt.*—1. Formed by precipitating the aqueous solution of *b* with alcohol.—2. By digesting orpiment with excess of sulphide of barium and water. When prepared by the first method, it separates in scales. Dissolves with difficulty in water, and, when the solution is left to evaporate spontaneously, it is again deposited in delicate white scales, with which very small transparent crystals of sulphate of baryta are mixed.

b. Bibasic Salt.—The nearly colourless aqueous solution dries up to a gummy mass, which when perfectly dry, exhibits a fine red-brown colour and redissolves completely in water. (Berzelius.)

E. SULPHARSENIATE OF BARIUM.—*a. Terbasic Salt.*—1. Formed when the salt *b* is heated to redness in a retort; sulphur and orpiment then sublime, and there remains a fused mass which assumes a brown colour on cooling. This substance dissolves in water, with the exception of a small quantity of brown matter, and the solution dries up to a crystalline, lemon-yellow mass.—2. By mixing *b* with sulphide of barium dissolved in water. This mixture, if cooled down to the freezing point in vacuo over oil of vitriol, and then left in the vacuum till the ice is evaporated, leaves the salt *a* in loose, transparent, non-crystalline scales. —3. On mixing the aqueous solution of *b* with alcohol, a white curdy substance is precipitated, easily soluble in water, and probably consisting of the same compound, but in the hydrated state.

b. Bibasic Salt.—The aqueous solution dries up to a fissured, lemon-yellow mass, which, if exposed to the air after all its water has been driven off, absorbs water again, swelling up and falling to pieces at the same time; it is soluble in water in all proportions. Sulphate of potash added to the solution throws down sulphate of baryta, while the corresponding potassium compound remains in solution.

c. Monobasic Salt.—Left in solution when *b* is precipitated by alcohol. The solution when evaporated deposits *a* and is thereby converted into *b*.

d. With 12 *atoms of acid.*—Yellow powder, which is decomposed by acids with evolution of sulphuretted hydrogen, and is not soluble in water.

ARSENIC AND STRONTIUM.

A. ARSENITE OF STRONTIA.—Saturated strontia-water is not precipitated by aqueous arsenious acid in any proportion, not even on boiling. (Gmelin.) Arsenite of potash precipitates chloride of strontium, but not till after some days, and more slowly than chloride of barium. (H. Rose.)

B. ARSENIATE OF STRONTIA.—*a. Di-arseniate.*—Formed by mixing strontia-water with a slight excess of arsenic acid, or chloride of strontium with di-arseniate of soda. Chloride of strontium is not precipitated by arsenic acid. White powder, insoluble in water.

b. Mono-arseniate?—The salt *a* is easily soluble in aqueous arsenic acid.

C. HYPOSULPHARSENITE OF STRONTIUM.—Analogous to the barium compound. (Berzelius.)

D. SULPHARSENIATE OF STRONTIUM.—*a. Terbasic Salt.*—Formed by precipitating *b* with alcohol. The precipitate sometimes forms a syrup, sometimes a white powder, accordingly as it is more or less purified from *b*; it dissolves easily in water.

b. Di-acid Salt.—Analogous to the barium compound. (Berzelius.)

ARSENIC AND CALCIUM.

A. ARSENITE OF LIME.—*a. Di-arsenite.*—Precipitated in flakes on mixing aqueous arsenious acid with excess of lime-water, or arsenite of ammonia with hydrochlorate or sulphate of lime. To obtain it pure, a bottle is completely filled with the mixture of arsenious acid and excess of lime-water, and then closed; afterwards the liquid decanted—the bottle filled up with water—the liquid decanted again, and so on, several times;

the precipitate is then collected on a filter—washed with a small quantity of water—and afterwards perfectly dried and preserved in a well-stopped bottle to prevent it from absorbing carbonic acid from the air. (Fr. Simon, *Pogg.* 40, 117.) White, heavy, coherent, powder.

	Dehydrated.		
$2CaO$	56	36·13	37·7
AsO^3	99	63·87	62·3
$2CaO, AsO^3$	155	100·00	100·0

	Dried in the air.		Simon.
$2CaO$	56·0	34·14	34·8
AsO^3	99·0	60·37	57·5
HO	9·0	5·49	7·7
$2CaO, HO, AsO^3$	164·0	100·00	100·0

Simon's analysis gives ½ At. water more; it is possible, however, that the salt, after drying in the air, may have had hygroscopic water adhering to it.

The salt, when heated to redness, gives off arsenic and is converted into arseniate of lime. For the complete decomposition of the arsenite of lime, long continued ignition is necessary; and the process succeeds better in the open air than in closed vessels. (Simon.) The salt attracts carbonic acid from the air. When it is mixed with solution of carbonate or phosphate of ammonia, potash, or soda, double decomposition takes place, the products being carbonate or phosphate of lime and soluble arsenite of ammonia, potash, or soda. In carbonate of ammonia it dissolves at first, but the solution soon becomes turbid. (Wittstein.) It dissolves readily in sulphate, hydrochlorate, nitrate, and acetate of ammonia (Gieseke & Schweigger, *Schw.* 43, 359); also in succinate of ammonia (Wittstein); also in arsenite of ammonia, if the latter does not contain too great an excess of alkali. (Schweigger.) The act of solution in heated ammoniacal salts is attended with evolution of ammonia. (Wach.) If freshly precipitated arsenite of lime in excess be digested in a concentrated solution of sal-ammoniac, a filtrate is obtained which yields no crystals even on the addition of alcohol, but when evaporated in the air, leaves a deliquescent residue of chloride of calcium and arsenite of lime with excess of arsenious acid. Similarly, arsenite of lime, when digested in arsenite of ammonia, forms a solution which is not precipitated by alcohol, but on evaporation yields acid arsenite of lime which is soluble in water. (Wach, *Schw.* 59, 272.) After drying, the arsenite of lime is less easily soluble in ammoniacal salts, but regains its original solubility on boiling. (Gieseke.) Diarsenite of lime is very sparingly soluble in pure water; about 3000 or 4000 parts of chloride of potassium or sodium dissolved in the water slightly increase the solubility. It dissolves readily in acids, even when weak and dilute.

b. Mono-arsenite.—A solution of chloride of calcium is mixed with aqueous ammonia saturated as much as possible with arsenious acid while hot; more ammonia is then added, whereby the precipitate is increased; and the precipitate is finally washed upon a filter. A considerable quantity dissolves during the washing. The precipitate when dry is lighter than *a.* When strongly ignited in the air, it gives off more than 22 per cent. of arsenic. It is somewhat soluble in water. (Simon, *Pogg.* 40, 417.)

	Dehydrated by heat.		Simon.
CaO	28	22·05	21·47
AsO^3	99	77·95	78·53
CaO,AsO^3	127	100·00	100·00

	Dried in a current of air.		Simon.
$2CaO$	56	21·29	20·74
$2AsO^3$	198	75·29	75·86
HO	9	3·42	3·40
$+\frac{1}{2}Aq.$	263	100·00	100·00

c. Acid Salt.—Formed by dissolving *a* or *b* in arsenious acid. Lime-water gives no precipitate with excess of arsenious acid.

B. ARSENIATE OF LIME.—*a. Tris-arseniate.*—1. Precipitated on mixing chloride of calcium with di-arseniate of ammonia, potash, or soda, the supernatant liquid acquiring an acid re-action. (Mitscherlich.) The supernatant liquid becomes slightly turbid on the addition of ammonia. (Wach.)—2. Precipitated on mixing chloride of calcium with tris-arseniate of soda. If the quantity of soda-salt added be insufficient to precipitate the whole of the lime-salt, the precipitate obtained is comparatively purer and less gelatinous: if, on the contrary, the lime-salt be added to an excess of arseniate of soda, the precipitate has a more gelatinous consistence, because it carries down with it a portion of the arseniate of soda. (Graham, *Pogg.* 32, 49.) The salt is decomposed when ignited alone: when ignited with sulphuric acid, it does not give up the whole of its arsenic acid. (Simon.)

b. Di-arseniate.—Found native in the hydrated state, as *Pharmacolite* and *Haidingerite.* Precipitated on mixing arsenic acid with lime-water in such proportion that the liquid may still contain a quantity of acid salt. *Haidingerite* is found in crystals belonging to the right prismatic system, and of specific gravity 2·848. (Haidinger, *Pogg.* 5, 181.) Pharmacolite occurs in capillary crystals—rarely in large crystals—belonging to the right prismatic system, and of specific gravity 2·73. Artificially prepared di-arseniate of lime is a white powder. The salt is not decomposed by heat, however intense. When digested in oxalate of ammonia, it is converted into oxalate of lime. (Laugier.) Insoluble in water; dissolves in hydrochloric and nitric acid, and likewise in aqueous sulphate, hydrochlorate, nitrate, and acetate of ammonia. (Pfaff, *Schw.* 45, 100.) The quantity dissolved by ammoniacal salts at ordinary temperatures is but slight, and the solution, after a while, deposits crystals of arseniate of lime and ammonia; but on boiling, the arseniate of lime is permanently dissolved, with evolution of ammonia. (Wach.) Vid. *Formation of Arseniate of Lime and Ammonia* (p. 306).

	Ignited.	*Artificial.*	Laugier.
$2CaO$	56	32·75	32·5
AsO^5	115	67·25	67·5
$2CaO,AsO^5$	171	100·00	100·0

	At.	*Haidingerite.*		Turner.
CaO	2	56	28·28	85·68
AsO^5	1	115	58·08	
HO	3	27	13·64	14·32
	1	198	100·00	100·00

	At.	*Pharmacolite.*		Rammelsberg.	Klaproth.
CaO	2	56	24·89	23·59	25·00
AsO^5	1	115	51·11	51·58	50·54
HO	6	54	24·00	23·40	24·46
CuO and Fe^2O^3				1·43	
	1	225	100·00	100·00	100·00

The *Pharmacolite* of Glücksbrunn analyzed by Rammelsberg is mixed with cobalt-bloom.

c. Mono-arseniate.—*a* and *b* are soluble in aqueous arsenic acid; the solution yields small crystals on evaporation.

C. Hyposulpharsenite of Calcium.—Red-brown powder, insoluble in water. (Berzelius.)

D. Sulpharsenite of Calcium.—*a. Terbasic Salt.*—When a solution of sulphide of calcium in the aqueous solution of *b* is mixed with alcohol, this salt is precipitated in the form of a white crystalline substance, while the compound *b* remains dissolved in the liquid. (Berzelius.) Voigt and Göttling (*Taschenb.* 1781, 49), by boiling 1 part of lime and 2 parts of orpiment with water, and setting the filtrate aside, obtained long needles which had a caustic taste. These crystals, when ignited, diminished in weight by 25 per cent., and became white and opaque without fusing; when treated with acids, they evolved sulphuretted hydrogen and yielded a precipitate of orpiment; they were soluble in water, but not in alcohol.

	Crystallized.		Or:			Berzelius.
3Ca	60	16·40	3CaS	108	29·51	29·80
As	75	20·49	AsS^3	123	33·61	33·55
6S	96	26·23	15HO	135	36·88	36·65
15HO	135	36·88				
$3CaS,AsS^3+15Aq$	366	100·00		366	100·00	100·00

b. Bibasic.—Formed by digesting orpiment with hydrate of lime and water, and filtering the solution from the arsenite of lime which is precipitated at the same time. The colourless filtrate, when left to evaporate in the air, deposits feathery crystals of the salt *a*, and between these the solution of *b* dries up to a brown amorphous mass. When the solution is macerated with excess of orpiment, it takes up rather a larger quantity of that compound, turning yellow and depositing a brown powder; if it be then left to evaporate freely, it acquires a light red-brown colour, and leaves a mass from which water extracts sulpharseniate of calcium, while hyposulpharsenite of calcium remains behind: the above-mentioned yellow solution, when mixed with alcohol before evaporation, gives a precipitate which soon turns brown.

E. Sulpharseniate of Calcium.—*a. Terbasic.*—$3CaS,AsS^5$.—Formed by digesting the aqueous solution of *b* with sulphide of calcium, and either evaporating the liquid or precipitating by alcohol. Not crystallizable: when precipitated by alcohol, it forms sometimes a powder, sometimes a syrup, according to the quantity of water which it contains. Easily soluble in water, but insoluble in alcohol.

b. Bibasic.—$2CaS,AsS^3$.—Precisely analogous to the barium compound. Dries up to a clear, faintly-coloured syrup, which, when further evaporated in the air, turns yellow at the edges, and finally solidifies to a yellow opaque mass. This substance loses its water at 60°, but recovers it again when exposed to the air, swelling up and cracking at the same time, and detaching itself from the glass vessel which contains it. Dissolves easily and without decomposition both in water and in alcohol. The syrupy aqueous solution does not crystallize or solidify even at $-10°$. When *b* is distilled at a red heat, there remains a colourless residue which appears to consist of $4CaS,AsS^5$, and, when roasted, in the air, is converted into an almost equal weight of gypsum. The aqueous solution of *b*, when boiled with pentasulphide of arsenic, takes up scarcely any of that compound. (Berzelius.)

F. Arseniate of Lime and Ammonia.—*Formation.*—When lime-water is mixed with a dilute solution of arseniate of ammonia, potash, or soda, and hydrochlorate, nitrate or acetate of ammonia, no precipitate is formed at first, but after a while, the double salt separates in needles. If the solution is more concentrated, lime-water immediately produces a copious precipitate, which, when digested in excess of the ammoniacal salt, does not dissolve, but becomes crystalline. If to a solution of 20 grains of sal-ammoniac in 2 ounces of lime-water, there be added a drop of arseniate of ammonia or potash, a precipitate is produced which soon disappears, and, in its place, crystals of the double salt make their appearance after a while; if several drops of the alkaline arseniate are added, a permanent crystalline precipitate is formed. On adding arsenious acid to lime-water till a strong turbidity is produced and then adding an ammoniacal salt, the liquid first becomes clear and afterwards deposits crystals of the double salt. Di-arseniate of lime immersed in solution of sal-ammoniac takes up one atom of ammonia, thereby rendering the liquid acid, and is converted into the same salt.

Preparation.—One part of arseniate of ammonia and 1 part of sal-ammoniac are dissolved in 4 parts of water, and lime-water added in successive portions, as long as crystals continue to form; the crystals, which increase in quantity when the liquid is set aside for 24 hours in a cool place, are afterwards washed on a filter with water, and dried between bibulous paper.

The salt crystallizes either in needles united together in stellated masses, or else in rhombic tables laid one upon another like steps. The crystals when exposed to the air, effloresce and lose their transparency. When heated, they evolve water, ammonia [nitrogen gas], and arsenious acid, while arseniate of lime remains behind. With moist lime they give off ammonia. They are slightly soluble in water and in solution of sal-ammoniac, easily in nitric or hydrochloric acid; ammonia added to the solution throws down the salt in the crystalline form, but not till after some time, if the liquid is dilute. (Wach, *Schw.* 59, 285.)

			Wach.
NH^3	17	5·41	5·35
$2CaO$	56	17·84	17·52
AsO^5	115	36·62	35·83
$14HO$	216	40·13	41·15
$NH^4O,2CaO,AsO^5 + 13Aq$	314	100·00	99·85

The resemblance of this compound to the phosphate of magnesia and ammonia, leads to the supposition that the quantity of water which it contains does not exceed 13 atoms.

ARSENIC AND MAGNESIUM.

A. ARSENITE OF MAGNESIA.—Magnesia heated to redness in a glass tube, absorbs the vapours of arsenious acid passed over it, without liberating arsenic. The compound only evolves arsenic when it is very strongly ignited, and is thereby partly converted into arseniate of magnesia. (Simon, *Pogg.* 40, 436.)

B. ARSENIATE OF MAGNESIA.—*a. Di-arseniate.*—Formed by precipitating hydrochlorate or sulphate of magnesia with di-arseniate of soda. —White powder, insoluble in water, but soluble in nitric acid.—The precipitate obtained by mixing dilute solutions of 3 parts sulphate of magnesia and 5 parts di-arseniate of soda, contains, on the whole, 15 atoms of water; of these, 12 atoms escape at 100°; the precipitate, therefore, consists of $2MgO, HO, AsO^5 + 2Aq. + 12Aq.$ By exposure to a bright red heat, it becomes insoluble in acids. (Graham, *Ann. Pharm.* 29, 24.)

b. Mono-arseniate.—Gummy, soluble in water.

C. HYPOSULPHARSENITE OF MAGNESIUM.—Brown powder, like the corresponding barium compound. (Berzelius.)

D. SULPHARSENITE OF MAGNESIUM.—The aqueous solution becomes light brown on evaporation, and dries up to a clammy syrup, and afterwards to a hard mass, which is permanent in the air, and, with the exception of a small quantity of the compound C that may be mixed with it, redissolves in water without further decomposition; it is likewise soluble in alcohol. The compound C is deposited, not only when the aqueous solution of the salt is evaporated, but likewise when a concentrated solution is cooled down to —5°, crystals of the compound E being deposited at the same time. (Berzelius.)

E. SULPHARSENIATE OF MAGNESIUM.—*a. Terbasic.*—$3MgS, AsS^5$.—Bihydrosulphate of magnesia is added to a solution of *b* as long as hydrosulphuric acid continues to be evolved, and the solution afterwards evaporated, or, if it be not too dilute, cooled quickly down.—Colourless, radiating crystals, which become moist on exposure to the air. Alcohol extracts from them the compound *b*, and leaves a compound of 1 At. AsS^5, with more than 3 At. MgS, which is nearly insoluble in water; the same compound remains behind, in the form of a white, porous, unfused mass, when *b* is heated to redness in a retort. Potash added to the aqueous solution of *a* precipitates magnesia, and converts the salt into a solution of the corresponding potassium compound.

b. Bibasic.—Non-crystalline, lemon-yellow mass, which is permanent in the air, does not absorb water from the air, dissolves in water in all proportions, and is not precipitated from the solution by alcohol. (Berzelius.)

F. ARSENIATE OF MAGNESIA AND AMMONIA.—Formed by adding a solution of tris-arseniate of ammonia to sulphate, nitrate, or hydrochlorate of magnesia, as long as a translucent crystalline precipitate continues to form, and afterwards washing and drying the precipitate. It effloresces slowly in the air, dissolves with great difficulty in water, but easily in acids. (Wach, *Schw.* 59, 288.)

			Wach.
NH^3	17	5·88	5·88
2MgO	40	13·84	13·93
AsO^5	115	39·79	39·45
13HO	117	40·49	40·74
$NH^4O, 2MgO, AsO^5 + 12Aq.$	289	100·00	100·00

¶ Levol (*Ann. Chim. Phys.* 17, 501) has obtained the same salt, with 10 atoms of water, by mixing a solution of magnesia containing sal-ammoniac, with an ammoniacal solution of arseniate of ammonia. It separates in small crystals. Loses 44·26 per cent. by ignition, the residue consisting of $2MgO, AsO^5$. ¶

G. SULPHARSENIATE OF MAGNESIUM AND AMMONIUM.—$NH^4S, 2MgS, AsS^5$?—Obtained by adding alcohol to an aqueous solution of the mixed sulpharseniates of ammonium and magnesium. After a few seconds, the terbasic compound is precipitated in delicate white needles. By exposure to the air, it is slowly converted into the bibasic salt (by loss of hydrosulphuric acid), and turns yellow. It is easily soluble in water. The aqueous solution, when left to spontaneous evaporation, gives off hydrosulphate of ammonia, and dries up to a yellow, non-crystalline mass, from the aqueous solution of which the terbasic compound may be again precipitated by alcohol. (Berzelius.)

H. ARSENIATE OF LIME AND MAGNESIA.—*Berzeliite.*—Specific gravity 2·52; white; of waxy lustre; easily pulverized. Before the blowpipe, it turns grey without melting or losing water. With borax and microcosmic salt it froths up, gives off an odour of arsenic, and forms a clear glass. With soda it effervesces, and forms a mass slightly coloured green by manganese. Perfectly soluble in nitric acid. (Kühn, *Ann. Pharm.* 34, 211.)

	At.	*Berzeliite.*		Kühn.
CaO	15	420	22·27	23·22
MgO	14	280	14·84	15·68
MnO	1	36	1·91	2·13
AsO^5	10	11·50	60·98	58·51
CO^2	(and a trace of Fe^2O^3)			0·30
		1886	100·00	99·84

$(3CaO, AsO^5) + (3MgO, AsO^5)$; part of the magnesia is replaced by manganous oxide.

Picropharmacolite is hydrated arseniate of lime and magnesia, but contains a large excess of magnesia, and cannot be reduced to any simple stoïchiometrical formula.

ARSENIC AND CERIUM.

A. CEROUS ARSENIATE.—*a. Bibasic.*—Formed by digesting cerous oxide in aqueous arsenic acid.—White powder insoluble in water.

b. Monobasic?—By dissolving *a* in excess of arsenic acid, a liquid is obtained, which does not crystallize on evaporation, but yields a transparent and colourless jelly. (Hisinger & Berzelius.)

B. CEROUS HYPOSULPHARSENITE.—A compound of bisulphide of arsenic with protosulphide of cerium. Preparation, similar to that of the corresponding barium compound. Red. (Berzelius.)

C. CEROUS SULPHARSENITE.—*Bibasic.*—2CeS, AsS^3.—The solution of disulpharsenite of sodium forms an orange-yellow precipitate with cerous salts. This precipitate acquires a finer colour on drying. When heated to commencing redness, it fuses to a transparent substance, which loses part of its sulphur-acid, but remains liquid and transparent as long as the heat is continued. By roasting in the air, it is readily converted into sulphate. Very slightly soluble in water, to which it imparts a yellow colour. (Berzelius.)

D. CEROUS SULPHARSENIATE.—*Terbasic and Bibasic Salts.*—Formed by precipitating a cerous salt with terbasic or bibasic sulpharseniate of sodium.—In both cases, a pale yellow precipitate is formed, which acquires a brighter colour when dry. (Berzelius.)

E. CERIC SULPHARSENIATE.—$2Ce^2S^3 + 3AsS^5$.—By precipitating a ceric salt. Yellowish white precipitate, slightly soluble in water, and therefore not appearing if the solutions are very dilute.

ARSENIC AND YTTRIUM.

A. ARSENIATE OF YTTRIA.—*a. Terbasic?*—By treating *b* with ammonia. (Berzelius.)—The same salt is obtained by precipitating a salt of yttria with di-arseniate of soda; the white precipitate dries up to yellowish brown, horny lumps, which, when treated with nitric acid, first become gelatinous and then dissolve.

b. Bibasic?—By adding a salt of yttria to di-arseniate of soda in excess.—White heavy precipitate, which becomes somewhat dark on drying, is easily soluble in nitric acid, and is left behind as a crystalline crust when the acid evaporates. (Berlin.)

c. Monobasic?—Aqueous arsenic acid dissolves yttria; on heating the solution, arsenic acid is precipitated in the form of a white powder. (Ekeberg.)

B. SULPHARSENITE OF YTTRIUM.—The saturated solution of orpiment in hydrosulphate of soda gives with salts of yttria a light yellow precipitate, part of which remains in solution and colours the liquid yellow; no sulphuretted hydrogen is evolved. The precipitate is yellow even after drying; it gives off but a small quantity of sulphuretted hydrogen when treated with acids. Ammonia decomposes it with separation of yttria. (Berzelius.)

C. SULPHARSENIATE OF YTTRIUM.—When hydrate of yttria is digested with water and pentasulphide of arsenic, small quantities of the two substances are dissolved, the liquid acquiring a yellow colour, and yielding a precipitate when treated with acids. A solution of terbasic or bibasic sulpharseniate of sodium produces no turbidity in solutions of yttria-salts. (Berzelius.)

ARSENIC AND GLUCINUM.

A. ARSENIDE OF GLUCINUM.—These two metals, when heated together, unite without visible combustion, and form a fused, grey, pulverulent alloy, which, when treated with water, evolves arseniuretted hydrogen. (Wöhler.)

B. ARSENIATE OF GLUCINA.—The bibasic salt is insoluble in water, but dissolves in excess of arsenic acid, forming an uncrystallizable *acid* salt. (Berzelius.)

C. and D.—SULPHARSENITE and SULPHARSENIATE OF GLUCINUM.—Analogous to the yttrium compounds. (Berzelius.)

ARSENIC AND ALUMINUM.

A. ARSENIDE OF ALUMINUM.—When a pulverulent mixture of the two metals is heated to redness, combination takes place with slight incandescence, and a dark grey powder is formed, which assumes the metallic lustre when rubbed, smells slightly of arseniuretted hydrogen, and evolves that gas slowly in cold, but rapidly in warm water. (Wöhler, *Pogg.* 11, 161.)

B. ARSENIATE OF ALUMINA.—*a. The more neutral salt.*—Formed by double decomposition.—White powder, soluble in acids but not in pure water.—From the solution of this salt in hydrochloric acid, sulphite of ammonia precipitates hydrate of alumina on boiling, the whole of the arsenic remaining dissolved in the form of arsenious acid. (Berthier, *N. Ann. Chim. Phys.* 7, 76.)

b. Acid Salt.—Soluble in water, but not crystallizable.

[The combinations of sulphide of aluminum with sulphide of arsenic are not satisfactorily made out. (Berzelius.)]

ARSENIC AND THORINUM.

ARSENIATE OF THORINA.—By double affinity.—White, flocculent precipitate, insoluble in water and in aqueous arsenic acid. (Berzelius.)

ARSENIC AND ZIRCONIUM.

A. ARSENIATE OF ZIRCONIA.—By double affinity.—Precipitate insoluble in water. (Berzelius.)

B. HYPOSULPHARSENITE OF ZIRCONIUM. — $2ZrS{,}AsS^2$. — Hyposulpharsenite of potassium dissolved in water gives with salts of zirconia, a dark brown, translucent precipitate, which slowly settles to the bottom of the liquid. (Berzelius.)

C. SULPHARSENITE OF ZIRCONIUM.—The saturated solution of orpiment in hydrosulphate of soda gives with zirconia-salts, an orange-yellow precipitate, which becomes darker on drying, and is not decomposed by acids; the supernatant liquid is yellow, because it holds a little of this compound in solution. (Berzelius.)

D. SULPHARSENIATE OF ZIRCONIUM.—The aqueous solution, either of the terbasic or bibasic sodium compound, gives with zirconia-salts (after a few minutes), a lemon-yellow precipitate, which becomes orange-yellow on drying, and, like sulphide of zirconium, is not decomposed by acids. (Berzelius.)

ARSENIC AND SILICIUM.

A. *Arseniate of Silica?*—Arsenic acid, fused in an earthen crucible, combines with the silica and forms a glass, which is soluble or insoluble in water, according to the amount of silica which it contains. According to Scheele, this glass contains arseniate of alumina. According to the same authority, also, aqueous arsenic acid has no action on hydrate of silica.

B. *Glass containing Arsenious Acid.*—A large proportion of arsenious acid gives a milky appearance to glass.

ARSENIC AND TITANIUM.

ARSENIATE OF TITANIC OXIDE.—Arsenic acid precipitates from salts of titanic oxide, white flakes resembling precipitated alumina, which dry up to a shining vitreous mass, and dissolve both in excess of the titanium solution and in excess of arsenic acid. If the titanium solution contains ferric oxide, that substance is precipitated at the same time. (H. Rose.)

ARSENIC AND MOLYBDENUM.

A. ARSENIATE OF MOLYBDOUS OXIDE.—Behaves exactly like the corresponding phosphate. (Berzelius.)

B. ARSENIATE OF MOLYBDIC OXIDE.—*a. Monobasic?* Formed by precipitating hydrochlorate of molybdic oxide with di-arseniate of soda.

b. Acid Salt.—The solution of hydrated molybdic oxide in excess of arsenic acid has a great inclination to turn blue, even when left to spontaneous evaporation. It forms with ammonia a deep red solution, which, when exposed to the air, deposits nothing, but becomes gradually decolorized. (Berzelius, *Pogg.* 6, 346.)

C. ARSENIATE OF MOLYBDIC ACID.—Molybdic acid, treated with arsenic acid, yields (*a*) a basic yellow compound, insoluble in water, and (*b*) a solution containing excess of arsenic acid. The latter, when evaporated to the consistence of a syrup, yields crystals. Alcohol decomposes these crystals, separating white flakes, which, however, are subsequently redissolved. The resulting alcoholic solution turns blue on evaporation, and yields no more crystals. (Berzelius, *Pogg.* 6, 383.)

D. Molybdic Sulpharsenite.—A compound of tersulphide of arsenic with tersulphide of molybdenum. When hydrosulphate of soda saturated with orpiment, is added to a solution of molybdic acid in hydrochloric acid, a dark brown powder is precipitated, which turns black on drying, and when distilled readily gives off orpiment [and sulphur?] and leaves bisulphate of molybdenum. (Berzelius.)

Aqueous sulpharseniate of sodium, mixed with solution of molybdic acid, forms a yellowish brown liquid, which gradually deepens in colour, but without forming a precipitate. (Berzelius.)

Arsenic and Vanadium.

A. Arseniate of Vanadic Oxide.—*a. Basic.*—Aqueous arsenic saturated with hydrate of vanadic oxide, yields, on evaporation, a gummy mass easily soluble in water, besides crystalline grains of *b*.

b. Acid Salt.—The solution of hydrated vanadic oxide in excess of arsenic acid, deposits, on evaporation, a crust of small, light-blue, crystalline grains, which may be freed from the acid mother-liquid by washing with water. The salt dissolves but very slowly, even in boiling water, or in water containing arsenic acid, but when once dissolved, no longer separates again on cooling; the addition of alcohol, however, precipitates it. Hydrochloric acid dissolves it quickly. (Berzelius.)

B. Arseniate of Vanadic Acid.—Formed by evaporating the solution of arseniate of vanadic oxide till it turns red and evolves nitric acid vapours. On cooling, a lemon-yellow compound separates, analogous to phosphate of vanadic acid. (Berzelius, *Pogg.* 22, 31, and 42.)

When sulphate of vanadic oxide is added to aqueous sulpharseniate of sodium, no precipitate is formed, but the blue solution becomes colourless. (Berzelius.)

Arsenic and Chromium.

Hydrochlorate of chromic oxide mixed with arsenite of ammonia gives no precipitate with free ammonia. (Bonnet, *Pogg.* 37, 303.)

A. Arseniate of Chromic Oxide.—Arseniate of potash gives an apple-green precipitate with salts of chromic oxide. (Moser.)

¶ When aqueous arsenious acid is added to a solution of monochromate of potash, the liquid acquires a fine green colour, and in a few minutes coagulates into a tremulous jelly, which, when dried at 100°, yields a substance whose empirical formula is $3AsO^5+4KO+3Cr^2O^3+10Aq$. If the liquids be mixed in the reverse order, the green colour is produced, but no precipitate. (Schweitzer, *J. pr. Chem.* 39, 267.) ¶

B. Chromic Sulpharsenite.—$2Cr^2S^3,3AsS^3$.—The saturated solution of orpiment in hydrosulphate of soda gives with salts of chromic oxide a dingy greyish-yellow precipitate, which turns greenish-yellow on drying. This precipitate melts when heated, giving off orpiment, and leaving a shining dark-grey residue, which yields a greenish-grey powder. This, when more strongly heated, gives off more orpiment and leaves a grey, pulverulent, soft compound which contains a large quantity of chromic sulphide with but little arsenious sulphide, and, when heated in the air, takes fire, gives off arsenious and sulphurous acid, and is converted into chromic oxide.

C. CHROMIC SULPHARSENIATE.—Salts of chromic oxide give a dirty yellow precipitate with the aqueous solution of terbasic or bibasic sulpharseniate of sodium.

ARSENIC AND URANIUM.

A. ARSENIATE OF URANOUS OXIDE.—*Terbasic.*—Formed by precipitating the solution of *b* in hydrochloric acid with excess of ammonia. Green, very bulky precipitate, which, after ignition, contains 66·73 per cent. of uranous oxide. *Bibasic.*—Hydrochlorate of uranous oxide is completely precipitated by di-arseniate of soda. The green precipitate, when heated, gives off 12·54 per cent. of water, and therefore consists of $2UO,AsO^5 + 4Aq$. On ignition, a few crystals of arsenious acid are sublimed from it, and uranic oxide is produced. It dissolves in hydrochloric acid more readily than the corresponding phosphate. (Rammelsberg, *Pogg.* 59, 26.)

B. ARSENIATE OF URANIC OXIDE.—Light yellow powder insoluble in water. (Berzelius.)

¶ According to Werther (*J. pr. Chem.* 13, 321) arsenic acid forms with uranic oxide two compounds analogous to the phosphates of that base (p. 17).

a. Di-arseniate. Prepared like the diphosphate. By precipitating uranic acetate with arsenic acid, a pale yellow salt is obtained, having the following composition:—

	Calculation.		Werther.
$2U^2O^3$	288	59·40	59·05
AsO^5	115	23·83	23·75
$9HO$	81	16·77	17·20
$(2U^2O^3, HO)AsO^5 + 8HO$	484	100·00	100·00

The salt loses 15·1 per cent. (8 atoms) of water at 120°.

b. Mono-arseniate.—Prepared by evaporating an excess of arsenic acid in contact with uranic oxide, acetate, or nitrate, and leaving the residue to dry over sulphuric acid. Small yellow crystals containing 5 atoms of water, 3 of which go off at 150°.

			Werther.
U^2O^3	144	47·25	48·2
AsO^5	115	37·92	38·2
$5HO$	45	14·83	14·0
$(U^2O^3, 2HO)AsO^5 + 3HO$	304	100·00	100·4

C. ARSENIATE OF URANIC OXIDE AND SODA.—When a solution of nitrate of uranic oxide is mixed with excess of basic arseniate of soda, $3NaO,AsO^5$, the whole of the uranic oxide is precipitated in the form of a pale yellow terbasic salt, in which one atom of uranic oxide is replaced by soda.

			Werther.
NaO	31·2	6·4	5·9
$2U^2O^3$	288·0	60·0	60·7
AsO^5	115·0	24·2	23·5
5HO	45·0	9·4	9·9
$(NaO, 2U^2O^3) AsO^5 + 5HO$	479·2	100·0	100·0

In Werther's analysis the arsenic acid was estimated by difference. All the alkalis, especially ammonia, have a great tendency to enter by substitution into the compounds of uranic oxide with phosphoric and arsenic acid. (Werther.) ¶

D. Uranic Sulpharsenite.—A compound of tersulphide of arsenic with sesquisulphide of uranium. Hydrosulphate of soda saturated with orpiment gives with uranic salts a deep yellow precipitate, which becomes greenish yellow on drying, and yields a dingy light-yellow powder. This precipitate when heated out of contact of air becomes semifluid, gives off part of its orpiment, and, after long continued ignition, is ultimately converted into an unfused, porous, greyish-brown mass, which appears to be a *more basic compound.* (Berzelius.)

E. Uranic Sulpharseniate.—Pentasulphide of arsenic with sesquisulphide of uranium. Aqueous terbasic or bibasic sulpharseniate of sodium precipitates from salts of uranic oxide, a dingy yellow substance, which appears deep yellow after drying, and dissolves in excess of sulpharseniate of sodium, forming a dark brown solution. (Berzelius.)

Arsenic and Manganese.

A. Arsenide of Manganese.—The native arsenide resembles Pyrolusite: sp. gr. 5·55; hard, greyish-white. When exposed to the air it becomes covered with a black powder. Fuses on platinum-foil and combines with the platinum. Before the blowpipe, it burns with a blue flame, emitting the garlic odour and producing white fumes of arsenious acid. Dissolves completely in aqua-regia and in large quantities of nitric acid. (Kane, *N. Quart. J. of Sc.* 6, 381; also *Pogg.* 19, 145.) Probably a mixture of the two metals.

			Kane.
2Mn	56	42·75	45·5
As	75	57·25	51·8
Fe			trace
Mn^2As	131	100·00	97·3

B. Arseniate of Manganous Oxide.—*a. Bibasic.*—Arsenic acid produces a turbidity in solution of acetate of manganous oxide, but not in the hydrochlorate. The salt is prepared: 1. By double decomposition. —2. By treating carbonate of manganous oxide with aqueous arsenic acid, the latter not being in too great excess. White, and, when prepared by (2), crystalline-granular. At a red heat, it does not decompose (Scheele, *Opusc.* 2, 66), but fuses to a dark red, very fluid glass, which does not give up its arsenic till it is treated with charcoal, but then gives up the whole of it. (Liebig, *Handwörterbuch,* 1, 507.) Insoluble in water, but soluble in nitric and sulphuric acid.

b. Monobasic.—Manganous salts are not precipitated by mono-arseniate of soda. (Pfaff.) The salt *a* dissolves in aqueous arsenic acid. (John.)

C. HYPOSULPHARSENITE OF MANGANESE.—Dark red precipitate. (Berzelius.)

D. SULPHARSENITE OF MANGANESE.—Hydrosulphate of soda saturated with orpiment precipitates from neutral manganous salts an aurora-red substance, which becomes darker on drying and yields an orange-red powder. When heated in close vessels, it gives off tersulphide of arsenic and is converted into a yellowish-green, pulverulent compound containing a large quantity of sulphide of manganese and a small quantity of orpiment. This compound is infusible and suffers no further decomposition by heat; when it is digested in hydrochloric acid, sulphuretted hydrogen is evolved, manganous oxide dissolved, and orpiment precipitated.

E. SULPHARSENIATE OF MANGANESE.—*a. Sexbasic.*—$6MnS,AsS^5$.—Formed by digesting the yellow powder of *b* in strong ammonia; pentasulphide of arsenic is then dissolved, and there remains a brick-red powder which is permanent in the air, has a pale brick-red tint when dry, is somewhat soluble in water, and, when ignited at one point, continues to burn.

b. Bibasic.—$2MnS,AsS^5$.—Formed by digesting freshly precipitated hydrated sulphide of manganese with water and pentasulphide of arsenic. The new compound partly dissolves in the water, partly remains at the bottom in the form of a yellow powder, which however dissolves in a larger quantity of water. The solution yields sulphur on evaporation, and afterwards deposits a lemon-yellow mass, which, from having undergone a certain amount of decomposition, no longer dissolves completely in water. Acids precipitate pentasulphide of arsenic from the solution and liberate hydrosulphuric acid. The same compound is obtained when carbonate of manganous oxide is boiled with water and pentasulphide of arsenic, but arseniate of manganous oxide is likewise formed at the same time. The aqueous solution of sulpharseniate of sodium does not precipitate manganous salts. (Berzelius.)

F. ARSENIATE OF MANGANOUS OXIDE AND AMMONIA.—When a mixture of chloride of manganese and ammonia is added to the aqueous solution of arsenic acid or arseniate of ammonia—especially if heat be applied—a flocculent precipitate is formed, consisting of manganous arseniate, which is soon converted into the crystallized double salt. This salt is washed with water deprived of air by boiling. Sometimes forms a reddish-white crystalline powder, sometimes small reddish crystalline grains. Permanent in the air. When heated, it gives off water and ammonia, and leaves di-arseniate of manganous oxide. With potash it evolves ammonia, forming arseniate of potash, and leaving di-arseniate of manganous oxide. Dissolves readily in dilute acids, but not in water or alcohol. (Otto, *J. pr. Chem.* 2, 414.)

			Otto.
NH^3	17	5·30	5·62
$2MnO$	72	22·43	22·81
AsO^5	115	35·82	36·89
$13HO$	117	36·45	34·68
$NH^4O,2MnO,AsO^5 + 12Aq$	321	100·00	100·00

The supposition that the salt contains only 12 atoms of water agrees most nearly with Otto's analysis; but he himself considers it as possible that the salt which he analyzed and which was dried at 16°, may have lost some of its water; with 13 atoms of water, this salt corresponds exactly to phosphate of magnesia and ammonia.

OTHER COMPOUNDS OF ARSENIC.

With Antimony, Bismuth, Zinc, Tin, Lead, Iron, Cobalt, Nickel, Copper, Mercury, Silver, Gold, Platinum, Palladium, and Rhodium—forming white, and mostly brittle and easily fusible alloys, which, when ignited out of contact of air, either retain their arsenic or give it up but partially—but if the air has access to them during ignition, evolve part of their arsenic in the form of arsenious acid, and retain the rest in the form of an arseniate of the metallic oxide. When ignited with nitre and carbonate of potash together, they yield arseniate of potash, and when ignited with potash-liver of sulphur they yield arsenical sulphur-salts of potassium, which may be washed out with water.

CHAPTER XXV.

ANTIMONY.

Bergmann. De antimonialibus sulphuratis. *Opusc.* 3, 164.
Thénard. *Ann. Chim.* 32, 257.
Proust. *A. Gehl.* 5, 543; also, *Gilb.* 25, 186.
Berzelius. Oxides of Antimony. *Schw.* 6, 144, and 22, 69.—Sulphide of Antimony. *Schw.* 34, 58.—*Pogg.* 20, 365; 37, 163.—Fluoride of Antimony. *Pogg.* 1, 34, and 200.
Berthier. Antimony and Sulphide of Antimony. *Ann. Chim. Phys.* 22, 239; and 25, 379.
H. Rose. Compounds of Antimony with Chlorine and Sulphur. *Pogg.* 3, 441.
Vauquelin. Antimonide of Potassium. *Ann. Chim. Phys.* 7, 32; also, *Schw.* 27, 219.
Serullas. Antimonides of Potassium and Sodium. *J. Phys.* 91, 123; 93, 115; also, *Ann. Chim. Phys.* 18, 217. Further, *Ann. Chim. Phys.* 21, 198; also, *Kastn. Arch.* 1, 113.
Pagenstecher. Metallic Antimonio-Sulphides. *Repert.* 14, 212.
Rammelsberg. Metallic Antimonio-Sulphides. *Pogg.* 52, 193.
Mitscherlich. *J. pr. Chem.* 19, 455; also, *Ann. Chim. Phys.* 73, 394.
Capitaine. *J. Pharm.* 25, 516; also, *J. pr. Chem.* 18, 449.
Liebig. *Handwörterbuch der reinen und angewandten Chemie*, 18, 449.
On Antimoniuretted hydrogen: L. Thomson. *Phil. Mag. J.* 10, 353; also, *J. pr. Chem.* 11, 369.—Pfaff. *Pogg.* 42, 339.—Simon. *Pogg.*

42, 369.—A. Vogel. *J. pr. Chim.* 13, 57.—Lassaigne. *J. Chim. Med.* 16, 638; 17, 440.—L. A. Buchner, *Repert.* 63, 250.

On Mineral-Kermes and Golden Sulphuret, *Alphabetically:* Brandes, *Br. Arch.* 37, 257.—*Schw.* 62, 209.—Buchner, *Repert.* 13, 169 and 203. —Bucholz, Junior, *Berl. Jahrb.* 29, 1, 26.—Cluzel, *Ann. Chim.* 63, 155.—Duflos. *Br. Arch.* 31, 94; 36, 278.—*Schw.* 62, 210; 67, 269. *Kastn. Arch.* 19, 61 and 289.—Fourcroy, *Crell. Ann.* 1788, 1, 423. —Fuchs, *Pogg.* 31, 578.—Gay-Lussac, *Ann. Chim. Phys.* 42, 87; also, *Schw.* 57, 252; also, *Pogg.* 17, 320.—Geiger, *Repert.* 9, 274.— *Mag. Pharm.* 29, 229.—Geoffroy, *Mém. de l'Acad. de Paris,* 1734, 593; 1735, 94.—Hennsmann, *Taschenb.* 1822, 184.—O. Henry, *J. Pharm.* 14, 545; also, *N. Tr.* 18, 2, 194.—Jahn, *N. Br. Arch.* 22, 43. —Liebig, *Mag. Pharm.* 35, 120; *Ann. Pharm.* 7, 1; 31, 57.—Otto, *Ann. Pharm.* 26, 88.—Pagenstecher, *Repert.* 14, 194, and 545.— Phillips, *Ann. Phil.* 25, 378.—Rammelsberg, *Pogg.* 52, 204.—Robiquet, *Ann. Chim.* 81, 317.—H. Rose, *Pogg.* 17, 324; 28, 481; 47, 323.—Schrader, *N. Gehl.* 3, 159.—Soubeiran, *J. Pharm.* 27, 294.— Thénard, *Ann. Chim.* 32, 257; also, *A. Tr.* 9, 1, 174.—Thomson, *Schw.* 17, 396; also, *Ann. Chim.* 93, 138.—Tromsdorff, *A. Tr.* 8, 1, 128.—A. Vogel, *Schw.* 33, 291.

Poggiale. *Compt. Rend.* 20, 1180; also *Ann. Pharm.* 56, 243.

Fremy. *N. Ann. Chim. Phys.* 33, 404; also *J. pr. Chem.* 45, 209.

Spiessglanz, Spiessglas, Spiessglanzkönig, Antimon, Antimonium, Stibium, Antimoine.

History. A few of the compounds of antimony appear to have been known to the ancients, but not antimony itself, the preparation of which, together with that of many of its compounds; was first described by Basilius Valentinus towards the end of the fifteenth century. The oxides, and many of the other compounds of antimony, were described by Proust, and more especially by Berzelius.

Sources. Rarely native;—as antimonic oxide; as antimonious acid or antimonic acid; as antimoniate of lime? very frequently as sulphide of antimony*; as sulphide of antimony in combination with other metallic sulphides: in Feather-ore, Jamesonite, Plagionite, Zinkenite, Boulangerite, Berthierite, Bournonite, Antimonial copper glance, Grey copper, Miargyrite, Dark red silver, Brittle sulphide of silver, Polybasite;—in combination with another metal: in arsenide of antimony, antimonide of nickel, and antimonide of silver: with another metal, together with a metallic sulphide in Nickeliferous grey antimony.

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* All the German and French sulphide of antimony occurring in commerce, excepting that from Montluçon, Department de l'Allier, contains from $\frac{1}{80}$ to $\frac{1}{20}$ of its weight of arsenic. Metallic antimony, flores antimonii, basic sulphate of antimonic oxide, kermes, sulphur auratum, vitrum, and crocus antimonii, antimonium diaphoreticum ablutum,—all these substances, prepared from sulphide of antimony containing arsenic, are contaminated with arsenic (the metallic antimony containing from $\frac{1}{50}$ to $\frac{1}{200}$ its weight, the kermes, $\frac{1}{300}$ to $\frac{1}{800}$); but crystallized tartar emetic (the arsenic remaining in the mother-liquor) and the powder of algaroth are free from this impurity. (Serullas, *Ann. Chim. Phys.* 18, 217.) The larger crystals of tartar emetic, however, which are principally formed in the mother-liquid, likewise contain arsenic. (Martius.)

Preparation.—1. Powdered grey sulphide of antimony, mixed with about half its weight of charcoal powder to prevent caking, is roasted at a gentle heat (on the small scale, on a roasting-dish; on the large scale, in a reverberatory furnace), with constant stirring, the fire being gradually increased, but not sufficiently to fuse the mass. The sulphur escapes in the form of sulphurous acid, and there remains a mixture of antimonious acid with a small quantity of antimonic oxide amounting to about ⅙ of its weight (Geiger & Reimann, *Mag. Pharm.* 17, 136), and traces of sulphide of antimony remaining undecomposed, the *Calx Antimonii grisea s. per se* or *Cinis Antimonii.* This residue is then mixed with half its weight of cream of tartar—or with 1 part of charcoal and ½ pt. potash—or with charcoal powder saturated with an aqueous solution of carbonate of soda—and fused in a covered crucible at a low red heat; the fused mass is then poured out into a hot mould partly filled with tallow, and the mould gently tapped to make the metal sink to the bottom. The slag at the top consists of a mixture of alkaline carbonate, double sulphide of antimony and potassium (or sodium) and charcoal. The charcoal separates the oxygen from the antimony and from a portion of the alkali; and the potassium or sodium thus eliminated separates the sulphur from part of the sulphide of antimony still present, and then, in the form of sulphide, unites with the remainder.—2. A mixture of 8 parts of sulphide of antimony and 6 parts of cream of tartar is heated in a crucible, nearly to redness, and from 2 to 3 parts of nitre are added till the mass becomes perfectly fused. Or a mixture of 8 pts. of sulphide of antimony, 6 pts. of cream of tartar, and 3 pts. of nitre, is projected by small portions at a time into a red-hot crucible placed in a furnace, and the whole heated for a short time, till perfectly fused. The mass is then poured out as before. The lower stratum consists of metallic antimony, the upper of double sulphide of antimony and potassium mixed with charcoal. The charcoal in the black flux (III. 20) withdraws oxygen from the potash; the potassium thus separated decomposes a portion of the sulphide of antimony, setting the metal free; and the resulting sulphide of potassium unites with the still undecomposed sulphide of antimony. Probably according to the following equation:

$$5SbS^3 + 6KO + 6C = 3(2KS, SbS^3) + 2Sb + 6CO.$$

According to this, only ⅖ of the antimony contained in the sulphide should be obtained in the metallic state, or 29·15 parts of regulus from 100 parts of the sulphide of antimony. This result accords with actual experience, 100 parts of sulphide of antimony being found to yield 27 parts of antimony. According to Liebig, however, by leaving out the nitre in this process, 100 parts of sulphide of antimony produce 45 parts of the metal.—3. An intimate mixture of 8 parts of sulphide of antimony with 1 pt. of dry carbonate of soda and 1 pt. of charcoal heated in an earthen crucible, and constantly stirred with a stick till it fuses quietly, and then poured out into the casting mould—yields 5·7 parts (71 per cent.) of antimony, which is afterwards purified from iron and copper by fusion with ⅛ its weight of nitre. (Duflos, *Br. Arch.* 36, 277; 38, 158.)—In this process, rather more than 3 atoms of carbonate of soda and charcoal are used to 1 atom of tersulphide of antimony, so that a sufficient quantity of sodium is set free to separate the whole of the sulphur:

$$SbS^3 + 3NaO + 3C = Sb + 3NaS + 3CO.$$

The fusion must be continued for a long time, during which the mass is very apt to boil over, and the antimony to burn away; the total amount obtained is only 66 per cent., and the antimony still contains the whole of the other metals which were present in the sulphide. (Liebig, *Mag. Pharm.* 35, 120.)—4. A mixture of 177 parts (1 at.) of sulphide of antimony with at most 82 parts (3 at.) of iron filings or iron nails is heated to bright redness in a closely covered crucible, and then left to cool.

$$SbS^3 + 3Fe = Sb + 3FeS.$$

The iron separates the whole of the sulphur, even at a gentle heat; but a stronger heat is required to fuse the sulphide of iron, and cause the antimony to form a distinct stratum beneath it; at this high temperature, the antimony is apt to burn away if the crucible be not well covered; hence a layer of charcoal powder over the mixture is useful.—The addition of carbonate of potash or soda, or of nitre, accelerates the fusion, because double sulphide of iron and potassium or sodium is thereby formed, which is more readily fusible than pure sulphide of iron. For example, 22 parts of nitre are added to a strongly ignited mixture of 100 parts of sulphide of antimony and 33 pts. of iron, or 6 parts of nitre to 100 parts of sulphide of antimony and 47 pts. of iron;—or 100 parts of sulphide of antimony, 42 pts. of iron, from 10 to 50 pts. of dry carbonate of soda, and 2 to 5 pts. of charcoal are melted together. Berthier, however, found it most advantageous to fuse together 100 parts of sulphide of antimony, 55....60 parts of smithy scales, 45 parts of carbonate of potash, and 10 parts of charcoal; this mixture yielded 69 parts of antimony; the mass however was found to froth up considerably. Liebig (*Mag. Pharm.* 35, 120) gives the preference to this method; but the regulus which it separates from sulphide of antimony containing lead, is contaminated with that metal. *Ann Pharm.* 22, 62.) A mixture of 100 parts of sulphide of antimony, 42 parts of iron, 10 parts of dry sulphate of soda, and 2½ parts of charcoal, yield between 60 and 64 parts of antimony. (Liebig, *Handwörterbuch*)—The slag obtained in the second process likewise yields a large quantity of antimony by fusion with iron, because the double sulphide of antimony and potassium is thereby converted into double sulphide of iron and potassium.

Antimony obtained by the first, second, and third processes,—the *Regulus Antimonii simplex s. vulgaris* which solidifies in the mould, and has a stellated structure on the upper surface, whence it has been called *Regulus Antimonii stellatus*—may contain sulphur, potassium, arsenic, lead, iron, and copper; the antimony prepared by the fourth method, *Regulus Antimonii martialis*, may contain a large quantity of iron, especially when the iron has been used in excess. The powdered antimony may be freed from iron by fusing it with sulphide of antimony; from sulphur, by fusion with carbonate of potash; from sulphur and potassium, by fusion with nitre; and, according to Berzelius, from sulphur, potassium, arsenic, and iron, by fusion with from ½ to 1 part of antimonic oxide.

By fusing sulphide of antimony, or the slag obtained in the second process, with tin, lead, copper, silver, &c., an antimony is obtained, which may contain small quantities of these metals; antimony thus prepared was formerly called *Regulus Antimonii jovialis, saturninus, venereus, lunaris,* &c.

Purification.—1. By the following method, commercial antimony and likewise that prepared on the small scale, may be perfectly freed from sulphur, arsenic, iron, (when not in too large quantity,) and copper, but not from lead; hence the antimony subjected to this process, must be previously freed from lead. A mixture of 16 parts of coarsely pounded antimony with 1 part of grey sulphide of antimony and 2 parts of dry carbonate of soda, is fused in a hessian crucible for an hour, care being taken to prevent any charcoal from falling into the mass. When cold, the crucible is broken, and the slag completely separated from the metal, which is again coarsely pulverized, fused with 1½ pt. dry carbonate of soda for an hour, and, lastly, after cooling and removal of the slag, once more fused with 1 part of carbonate of soda. In this manner, 15 parts of pure antimony are obtained. (Liebig, *Ann. Pharm.* 19, 22.) The sulphide of antimony converts the other metals, except the lead, into metallic sulphides, which pass into the slag in combination with sulphide of sodium. The remaining arsenic is separated by the carbonate of soda, in the form of arseniate of soda. If any charcoal falls into the crucible, it reduces arsenic from the arseniate of soda, whereby the antimony is again rendered impure. (Liebig.) Hence a black-lead crucible cannot be used; such a crucible also reduces sodium, which then mixes with the antimony. (Anthon, *Repert.* 59, 240.) If the commercial antimony has been prepared with iron, and is consequently richer in iron, a larger quantity of sulphide of antimony must be added in the first fusion, that is to say, in proportion nearly corresponding to the iron, (4 parts of sulphide of antimony and 4 parts of carbonate of soda, to 16 parts of the antimony); in this case the loss of antimony is greater. As long as iron is present, it is impossible to remove the arsenic by means of carbonate of soda. (Liebig, *Ann. Pharm.* 22, 58: *Handwörterb.* 1, 416.—See also Buchner, *Repert.* 51, 267.)—2. Well washed powder of algaroth is reduced with alkali and charcoal. By this means, all impurities from the heavy metals are got rid of. Artus (*J. pr. Chem.* 8, 127), digests 1 part of finely powdered grey sulphide of antimony or glass of antimony, with 2 parts of common salt, 3 parts of oil of vitriol and 2 parts of water for 8 hours; then boils for an hour, and afterwards mixes the liquid with water till a permanent precipitate begins to appear; then filters; precipitates the powder of algaroth by adding more water; washes it thoroughly; and fuses 100 parts of the dry compound with 80 parts of dry carbonate of soda and 20 parts of charcoal powder, for 15 or 20 minutes: 61 parts of pure antimony are thus obtained.—3. The purest antimony is obtained from tartar-emetic, purified by repeated crystallization. (Capitaine, *J. Pharm.* 25, 516; also *J. pr. Chem.* 18, 449.)

Purification from Arsenic only. 1. Four parts of pounded commercial antimony are mixed with 5 parts of nitre and 2 parts of dry carbonate of soda (without the latter, insoluble arseniate of antimonic oxide would be formed), and the mixture projected into a red-hot crucible. The mass remaining after the combustion (which takes place quietly), is then pressed together, heated for half an hour at a higher temperature, so that it may become pasty but not fused, and pressed down as often as it swells up from evolution of gas. After this, it is taken out of the crucible with the spatula, while still hot and soft, then reduced to powder, and boiled for some time in water with frequent stirring. The water, together with the finer powder, is then poured off; the coarser powder crushed with a pestle, and boiled with a fresh quantity of water; the two liquids with their deposits mixed; and the insoluble portion freed by repeated subsidence and decantation, and, lastly, by washing on a filter, from the alkaline solution which contains the alkaline arseniate and but a very small quantity of antimoniate. The washed acid antimoniate of potash is white; but if it contains lead, which cannot be removed by nitric acid, it has a yellow colour. It is then fused with half its weight of cream of tartar at a moderate red heat, and the resulting antimony containing potassium is pulverized and thrown into water, which removes the potassium and gives off pure hydrogen gas. (Wöhler, *Pogg.* 27, 628; also, *Ann. Pharm.* 5, 20.) ¶ According to C. Meyer, (*Ann. Pharm.* 66, 236; *Centr. Blatt.* 1848, 828,) the use of nitre is objectionable, because it gives rise to the formation of antimoniate of potash, which destroys the exactness of the process. Meyer recommends a mixture of nitrate and carbonate of soda, whereby a mass is obtained, which does not yield a trace of antimony to water. This method is so exact, that it may be used to separate antimony from arsenic in quantitative analysis; moreover, the antimony thus obtained is not contaminated with potassium or sodium. ¶ This method is good, but too expensive, and from the tedious washing of the antimoniate of potash, difficult of execution on the large scale. Moreover, the whole of the iron and copper, besides a small quantity of potassium, remains in the antimony. (Liebig.)—Göttling (*Taschenb.* 1780, 96) burned a mixture of 16 parts of sulphide of antimony and 20 parts of nitre; exhausted the mass with hot water; fused the residue, after drying, with 16 parts of cream of tartar; and obtained 9 parts of antimony, which probably was nearly free from arsenic.—2. One part of pulverized antimony, prepared by the second method, is rapidly fused with half its weight of carbonate of potash and the mass poured out; the metal obtained is then crushed, fused with one-fourth its weight of nitre; again poured out; the metal again crushed, and fused with one-third its weight of hydrated antimonic acid; and lastly, the antimony, after being repulverized, is fused with one-third its weight of carbonate of potash, and poured into the mould. This method completely removes the arsenic. (Th. Martius, *Kastn. Arch.* 24, 253.)—3. If 32 parts of antimony rich in arsenic, are fused with 4 parts of nitre, the slag contains a large quantity of arseniate of potash; the resulting 30 parts of metal fused with 3 parts of nitre, still yields a small quantity of arseniate of potash and 27 parts of metal; this, if again fused with 2 parts of nitre, yields a slag, containing scarcely anything but antimoniate of potash and metallic antimony, perfectly free from arsenic. If carbonate of potash be used instead of nitre, the separation of the arsenic is much more difficult. (J. A. Buchner, *Repert.* 44, 246.)—4. One part of antimony, prepared by the third method, is heated with 1½ pt. of oil of vitriol in a porcelain basin, stirring constantly as long as sulphurous acid gas continues to be evolved, and water carefully added by small portions at a time, till a greyish-white, intumescent mass is formed. This is mixed in a vessel made of antimony, with from 0·2 to 0·4 pt. finely powdered fluorspar, and 0·4 to 0·8 pt. oil of vitriol (according to the quantity of arsenic present). The whole is then heated, with constant stirring, as long as hydrofluoric acid and fluoride of arsenic are given off; the residue afterwards gradually mixed with water; washed by decantation, till the wash-water ceases to exhibit an acid reaction; and the remaining basic sulphate of antimonic oxide reduced by fusion with half its weight of cream of tartar, in a covered crucible. If a leaden vessel were used, antimony and arsenic would be reduced together, and consequently the antimony obtained would not be free from arsenic. (Duflos, *Kastn. Arch.* 19, 56; also, *Schw.* 60, 353; further, *Schw.* 62, 501; see also Buchner & Herberger, *Repert.* 38, 381; 44, 246.)

Tests for Impurities in Antimony.—1. *Sulphur.*—The powdered metal, when heated with strong hydrochloric acid, disengages hydrosulphuric acid.—2. *Potassium* or *Sodium.*—The antimony appears more grey than white, and loses its lustre on exposure to the air. Its powder has an alkaline taste, reddens moist turmeric paper, and evolves hydrogen gas when put under water, giving up alkali to the liquid.—3. *Arsenic.*—The metal, when fused in the air, emits a garlic odour. If its powder be detonated with about ¼ pt. nitre, and the resulting mass treated with water, a filtrate is obtained, which contains arseniate and antimoniate of potash, so that, when supersaturated with hydrochloric acid and rapidly saturated with hydrosulphuric acid gas, it first gives a yellowish-red precipitate of pentasulphide of antimony, and then if rapidly filtered and preserved in a close vessel, gradually deposits a yellow precipitate of pentasulphide of arsenic. The antimony ignited with an equal weight of cream of tartar in a covered crucible, yields an alloy of potassium, arsenic, and antimony, which, if reduced to powder under water, evolves arseniuretted hydrogen, recognizable by its depositing brown metallic arsenic on ignition (p. 265).—4. *Lead.*—The powdered metal boiled with nitric acid nearly to dryness, and then treated with water, yields a filtrate which contains nitrate of lead, and is consequently precipitated by sulphuric acid. When the quantity of lead is large, a solution of antimony in aqua-regia deposits crystalline needles of chloride of lead on cooling.—If the antimony contains sulphur besides the lead, the lead remains undissolved in the form of sulphate, on treating the metal with nitric acid. If the antimonic oxide in the residue is then dissolved out by warm hydrosulphate of ammonia, black sulphide of lead remains behind, and if iron is present, black sulphide of iron also.—5. *Iron.*—The finely divided metal ignited with 3 times its weight of nitre, and washed with boiling water, leaves a yellowish residue, from which boiling dilute hydrochloric acid separates ferric oxide, which may be detected by ferrocyanide of potassium, &c.—6. *Copper.*—When the lead has been precipitated from the nitric acid solution by sulphuric acid, according to the method above given, the cupric oxide remains dissolved, and may be recognized by its behaviour with hydrosulphuric acid, ferrocyanide of potassium, ammonia, or polished iron.

Pure antimony fuses before the blowpipe on charcoal, forming a shining globule which burns completely away with evolution of inodorous vapours, and becomes covered, on cooling, with beautiful white needles of antimonic oxide. Impure antimony, on the contrary, exhales a garlic odour, especially at the commencement; becomes covered with a slag of sulphide of iron; has a dull surface; ceases to burn as soon as the blowpipe flame is withdrawn; and yields a yellow oxide. (Liebig.) Pure antimony, after fusion before the blowpipe, should solidify in a smooth globule having a silvery lustre. (Capitaine.) A solution of antimony in aqua-regia should give a yellowish-red precipitate with hydrosulphate of ammonia, perfectly soluble in excess of the precipitant. If a black residue is left, it must consist of sulphide of lead, iron, or copper. (H. Rose.)

Properties.—Crystalline system the rhombohedral. Primary form an acute rhombohedron. *Fig.* 151; $r^3 : r^5 = 87° 39'$: also an obtuse rhombohedron (*Fig.* 141) the axis of which is half as long as that of the acute rhombohedron, and in which, according to Mohs, $r^3 : r^5 = 117° 15'$.

(Breithaupt, *Schw.* 52, 169.) When fused antimony is allowed to solidify partially and the fused portion then poured off, small acute rhombs approaching the cube, are obtained (*Fig.* 151) $r^3 : r^5 = 87^\circ 28'$, with one very distinct plane of cleavage parallel to *p* (*Fig.* 152), and three less brilliant, which cut off the vertical edges, and consequently tend to produce an obtuse rhombohedron (*e.g.* corresponding to the truncation-faces in *Fig.* 145). The angle between the principal cleavage-plane parallel to *p*, and one of the other three = 142° 5′. (Marx, *Schw.* 59, 211.) H. Rose (*Pogg.* 15, 454) and Elsner (*J. pr. Chem.* 20, 71) likewise obtained distinct rhombohedrons. Hauy formerly supposed that he had discovered in antimony the 4 cleavage-planes of the regular octohedron and the 6 cleavage-planes of the rhombic-dodecahedron. Sp. gr. = 6·7006 (Karsten), 6·702 (Brisson), 6·712 (Hatchett), 6·715 at 16° (Marchand & Scheerer), 6·723 (Böckmann), 6·860 (Bergman). If from pure antimony of specific gravity 6·715, a cylinder is filed so as exactly to fit a diamond mortar, and is then submitted therein to a pressure of 150,000 lbs., it is first crushed to powder, and afterwards re-converted into a perfectly solid mass which has a specific gravity of 6·714. Similarly, commercial antimony, of specific gravity 6·696, after being crushed and resolidified in a diamond mortar, has a specific gravity of 6·693. Hence antimony has the same specific gravity whether in the crystallized or in the compressed state. (Marchand & Th. Scheerer, *J. pr. Chem.* 27, 207.) Not very hard; very brittle, and easily reduced to powder. Tin-white, highly lustrous. Fuses at 432°, according to Dalton; at 513°, according to Guyton-Morveau. The purer the antimony, the more easily does it fuse. (Capitaine.) It does not dilate on cooling. (Marx, *Schw.* 58, 464.) Volatilizes out of contact of air only at very elevated temperatures, but in a current of air, much less heat is required. Antimony covered with a flux loses less than $\frac{1}{1000}$ of its weight in the strongest white heat; but, in a current of hydrogen gas, it may be distilled at a white heat. (Liebig. *Handwörterbuch.*)

Compounds of Antimony.

ANTIMONY AND OXYGEN.

A. SUBOXIDE OF ANTIMONY. SbO?

1. In moist air, antimony becomes covered with a thin film of suboxide, and is thereby rendered dull and of a darker grey colour.—2. When a bar of antimony is used for the positive electrode in the decomposition of water, it becomes covered with a lead-grey film, which appears blackish-grey after drying. To obtain the suboxide in larger quantity, powdered antimony is immersed in water, and connected by a platinum wire with the positive pole of a battery; and the bluish-grey flocculent powder which is formed, is separated, from time to time, from the rest of the antimony, by levigation. The suboxide when dry is blackish-grey, and cannot be made to take the metallic lustre by pressure with the burnisher. When treated with hydrochloric acid, it is resolved into antimonic oxide, which dissolves, and a residue of the metal. (Berzelius.) Regarded by Proust as a mixture of metal and oxide.

B. ANTIMONIC OXIDE. SbO^3.

Teroxide of Antimony, Protoxyde d'Antimoine.—Found native as *White Antimony Ore* (*Weiss-spiessglanzerz*) or *Flowers of Antimony.* (*Antimonblüthe.*)

Formation.—1. When antimony is heated in the air till it boils, it takes fire and burns with a bright bluish-white flame, and at a moderate red-heat with a reddish light,—yielding antimonic oxide, which condenses on cold bodies in the form of *Flowers of Antimony, Flores Antimonii argentei, Nix Stibii.* When strongly ignited antimony is thrown on the ground, it separates into small globules which continue to burn. Antimony heated to strong redness on charcoal before the blowpipe and then left to cool quietly, becomes covered with brilliant needles of antimonic oxide. If the antimony contains but a trace of arsenic, it emits the garlic-odour in burning. According to Liebig and Capitaine, it does not emit any odour when pure; but according to Pfaff, Wöhler, and Martius, it evolves a peculiar odour totally different from that of garlic, and compared by Martius to that of nitric acid.—2. When aqueous vapour is passed over antimony at a strong red-heat, hydrogen gas is set free and crystallized antimonic oxide formed. (Berzelius, Regnault, *Ann. Chim. Phys.* 62, 362.) The author did not succeed in evolving hydrogen by boiling antimony with strong hydrochloric acid.—3. In hot oil of vitriol, antimony is converted into sulphate of antimonic oxide, with evolution of sulphurous acid gas.—4. When the metal is treated with nitric acid, nitric oxide is disengaged, and a mixture of basic nitrate of antimonic oxide and antimonious or antimonic acid is formed. At the temperature of 20°, nitric acid perfectly free from nitrous acid does not attack antimony at any degree of concentration; only the strongest acid acting on it, slightly and without effervescence. Aqua-regia is likewise without action, when so dilute and cool that the two acids are not decomposed; but the addition of a few drops of nitrous acid induces the act of combination, which afterwards goes on by itself; a current of chlorine, on the contrary, does not set up the action. (Millon.) The colder and more dilute the nitric acid, the greater is the quantity of nitrate of antimonic oxide formed and the smaller that of the antimonious acid; but with the basic nitrate of antimonic oxide, a large quantity of metallic antimony remains mixed, and is left behind on dissolving the oxide in hydrochloric acid. That antimonious acid (antimoniate of antimonic oxide) and not antimonic acid is produced by the stronger action of nitric acid, is proved by the following fact. When a mixture of antimonic acid with pure antimonic oxide is boiled with cream of tartar and water, a turbid solution is obtained; but on substituting antimonious acid for the antimonic acid, a clear solution is formed, which first yields crystals of tartar emetic and then leaves a gummy residue. The powder obtained by acting on antimony with nitric acid exhibits the last-mentioned character. (H. Rose, *Pogg.* 53, 161.)—5. By fusing antimony with oxide of lead, antimonic oxide and metallic lead are formed. (Liebig.)—6. Antimonious or antimonic acid is converted into antimonic oxide by ignition with antimony or sulphide of antimony.

Preparation.—1. By burning antimony in an inclined crucible exposed to the air, and passing the ascending vapours through earthen or wide glass tubes, wherein the flowers of antimony are deposited. The necks of broken retorts or receivers make convenient tubes for this purpose. If the antimony is heated to redness in a wide crucible inclined and loosely covered, the conducting tube may be dispensed with, as the oxide sublimes in the cooler parts of the crucible, and even forms brilliant needles: these must be removed from time to time. By this process, 8 parts of metal yield more than 9 parts of oxide. (Liebig.) The oxide obtained by combustion contains however antimonious acid, which renders it difficultly fusible. (H. Rose.)—2. Oxy-chloride of antimony is digested with an aqueous solution of carbonate of potash or soda, and the residue thoroughly washed: 1 part of carbonate of soda to 20 parts of powder of algaroth. This process yields a pure oxide free from any higher oxygen-compound. (H. Rose.)—3. The sulphate of antimonic oxide, obtained by boiling powdered antimony with oil of vitriol to dryness, may be treated in a similar manner. By mere boiling with water, the acid is less completely removed; nevertheless, the greater part may be separated by water, so as to render a smaller quantity of alkali sufficient.—4. Pulverized antimony is boiled with moderately strong nitric acid till it is converted into a white powder, which is then freed from nitric acid by repeated boiling with pure water. The white powder is a mixture of basic nitrate of antimonic oxide, sometimes with antimony, sometimes with antimonious acid, and sometimes with both together (p. 324). The exact temperature and strength of the nitric acid necessary to convert the whole of the antimony into oxide without any admixture of antimonious acid, cannot be determined. At a moderate heat, more than $\frac{1}{2}$,—by boiling, $\frac{2}{3}$ of the antimony are converted into antimonious acid. But 1 part of powdered antimony digested with 2 parts of aqua-regia and 4 parts of water yields 96·6 per cent. of antimonic oxide after washing. (Brandes, *N. Br. Arch.* 21, 156.)—5. A mixture of 74 parts of antimony, 39 parts of nitre, and 34 parts of bisulphate of potash is projected into a red-hot crucible, the ingredients being added rapidly one after the other; the covered crucible is then kept red-hot for some time; and the resulting mass, in which needles of antimonic oxide are found, is boiled, first with pure water, then with water containing sulphuric acid, and lastly again with pure water. Any arsenic that may be present is dissolved in the first wash-water, but iron remains behind with the oxide. (Preuss, *Ann. Pharm.* 31, 197.)—6. Sulphide of antimony is roasted thoroughly, and the resulting antimonious acid fused with from $\frac{1}{20}$ to $\frac{1}{16}$ its weight of sulphide of antimony. (Berzelius.) With even a small excess of sulphide of antimony, oxysulphide of antimony (*Spiessglanzglas*, vid. seq.) is formed, but with a small deficiency of the sulphide, antimonious acid remains undecomposed and renders the glass turbid; when the exact proportions are observed, the glass is colourless and transparent.

If the antimonic oxide prepared by either of these processes contains a higher compound of the metal with oxygen, it evolves sulphurous acid when fused with sulphide of antimony in a tube through which hydrogen (or carbonic acid) gas is passed. (H. Rose.) Moreover, when dissolved in moderately dilute hydrochloric acid or in a hot solution of cream of tartar, it leaves a residue.

Properties.—Dimorphous.—*a.* The native oxide belongs to the right prismatic system (*Fig.* 65) $u^1 : u = 136° 58'$; $i : i = 70° 32'$; cleavage parallel to u. Sp. gr. = 5·56. (Mohs.) Hardness, equal to that of rock-salt. Colourless, translucent, with diamond-lustre, the t-face having a pearly lustre. By the first method, also, antimonic oxide is obtained in very brilliant needles of the same form, having, according to Boullay, a specific gravity of 5·778.—*b.* Sometimes, however, antimonic oxide sublimes in regular octohedrons instead of needles. (Bonsdorff & Mitscherlich, *Pogg.* 15, 453; Wöhler, H. Rose, *Pogg.* 26, 180.) If a few ounces of antimony are heated till they begin to burn, and then left to cool slowly, needles are obtained having octohedrons adhering to them. (Berzelius.) [Hence it would appear that antimony takes the octohedral form, when it sublimes at a comparatively low temperature.] According to Mitscherlich (*J. pr. Chem.* 19, 455; also *Ann. Chim. Phys.* 73, 394), these octohedrons may likewise be obtained in the wet way. From a solution of antimonic oxide in boiling soda, octohedrons separate on cooling the liquid in close vessels. A solution of tartar-emetic decomposed by ammonia, soda, or potash (which latter must not be in excess), or by alkaline carbonates, yields microscopic octohedrons after some time. The flocculent precipitate produced by pure alkalis or alkaline carbonates in acid hydrochlorate of antimonic oxide, is converted, sometimes during washing, sometimes on drying, into small octohedrons; but if the boiling acid hydrochlorate of antimonic oxide be added to a boiling solution of carbonate of soda, the oxide separates in the form of prisms. (Mitscherlich.) Antimonic oxide, by whatever method it may have been prepared, turns yellow every time it is heated, and fuses even at a low red-heat, forming a yellowish or greyish liquid, which on cooling solidifies to a white asbestos-like mass, having a silky lustre. At a higher temperature, it volatilizes—even in a glass tube, provided the air is excluded—and sublimes in needles. It acts as an emetic.

	Calculation.		Berzelius.	J. Davy.	Proust.
Sb	129	84·31	84·319	85	81·5
3O	24	15·69	15·681	15	18·5
SbO^3	153	100·00	100·000	100	100·0

($Sb^2O^3 = 2 \,.\, 806{\cdot}45 + 3 \,.\, 100 = 1912{\cdot}9$. Berzelius.)

Decompositions.—By potassium at a gentle heat, yielding metallic antimony, with evolution of light and heat. By charcoal it is reduced to metallic antimony; before the blowpipe on charcoal, it is reduced much more easily than antimonious or antimonic acid, and imparts a green tinge to the flame. (Berzelius.)—By carbonic oxide gas at a red heat, to metallic antimony. (Gmelin.)—Similarly by hydrogen gas (Liebig); by fused cyanide of potassium, the products being metallic antimony and cyanate of potash. (Liebig.)—By fusion with a small quantity of sulphur, sulphurous acid is evolved, and glass of antimony formed; but with a larger quantity of sulphur, sulphide of antimony is produced. (Proust.)

$$2SbO^3 + 9S = 2SbS^3 + 3SO^2.$$

By bihydrosulphate of ammonia, it is first converted into yellow saffron, and then into brownish-red kermes, part of which dissolves. (Berzelius.) —When it is boiled with sulphur and solution of caustic soda, sulphantimoniate of sodium and antimoniate of soda are formed. (Mitscherlich.) —It is not altered by fusion with antimony. (Proust.)

Combinations.—*a.* Antimonic oxide does not appear to form a definite hydrate, but, according to Berzelius, it is sparingly soluble in water.—

It dissolves sparingly in water, especially in boiling water, without separating as the liquid cools. The solution is coloured yellow by hydrosulphuric acid, and gives an orange-coloured precipitate, either after long standing, or immediately on boiling, or on the addition of hydrochloric acid. Ammonia decolorizes the solution treated with hydrosulphuric acid. (Capitaine.)

¶ According to Fresenius, the following method yields *Hydrate of Antimonic Oxide.* A solution of recently precipitated tersulphide of antimony in caustic potash is heated to the boiling point, and solution of sulphate of copper added, till a portion of the liquid, when mixed with acids, gives a pure white precipitate without any tinge of orange. The liquid is then filtered from the sulphide of copper, and treated with acetic acid as long as a precipitate is formed; the precipitate is lastly collected on a filter, washed, and dried. When gently heated, it lost 10·90....11·20 per cent. of water, corresponding to the formula SbO^3+2Aq.

	Calculation.			Fresenius.
SbO^3	153	....	89·474	89·95
2HO	18	....	10·526	11·05
SbO^3+2Aq	171	....	100·000	101·00

(L. Schaffner, *Ann. Pharm.* 51, 168.) ¶

b. With acids, forming the Salts of Antimonic Oxide, or Antimonic Salts.—These salts are obtained by bringing the acid in contact, either with the metal or with pure antimonic oxide, or with a substance containing antimonic oxide, such as the glass of antimony or antimonial saffron. They are colourless or yellowish, and have a faint metallic taste and strong emetic properties. They lose their acid at a red heat, if it be volatile. When mixed with carbonate of soda and fused on charcoal before the blowpipe, they yield metallic antimony. From their solution in water or acids, *e. g.*, from acid hydrochlorate of antimonic oxide, the whole of the antimony is precipitated in the form of a black powder, by zinc, cadmium, tin, lead, iron, or cobalt; bismuth and copper precipitate it but imperfectly. (Fischer, *Pogg.* 8, 499; 9, 264; *N. Br. Arch.* 11, 120.) The precipitated antimony takes fire when dried in the air, even at a gentle heat. (Liebig.) Copper becomes covered with a metallic, violet-coloured film in a solution of acid hydrochlorate of antimonic oxide diluted 200,000 times; also in a solution of tartar-emetic, after the addition of a small quantity of hydrochloric acid. (Reinsch, *J. pr. Chem.* 24, 247.)—Hydrosulphuric acid precipitates yellowish-red tersulphide of antimony from solutions of antimonic salts, even when they contain a large excess of acid,—according to Pfaff, in solutions of 1 part of salt in 20,000 parts of water.—One part of tartar-emetic dissolved in 10,000 parts of water and 5,000 parts of hydrochloric acid gives a slight cloudiness with hydrosulphuric acid; with 15,000 pts. of water and 7,500 pts. of hydrochloric acid, still a yellow colour; with 30,000 pts. of water and 15,000 pts. of acid, no visible effect is produced. (Reinsch, *J. pr. Chem.* 13, 132.)—Alkaline hydrosulphates produce the same yellowish-red precipitate; but if added in excess, they redissolve it, especially if heat be applied, or if an alkaline hydrosulphite is mixed with the precipitate, or if finely powdered sulphur is added to it. (H. Rose.)—Dilute solutions of antimonic salts give with hyposulphite of soda, on the addition of a small quantity of hydrochloric acid, a yellow precipitate, which gradually changes almost to cinnabar-red (the colour of kermes). (Himly.)—The affinity of antimonic oxide for acids is but feeble; the neutral compounds, unless mixed with tartaric acid, are frequently resolved by excess of water, into dilute acid holding a small quantity of antimonic oxide in solution, and a basic salt which falls to the bottom. The acid when supersaturated with water, appears to lose its affinity for the antimonic oxide; accordingly, the larger the quantity of water added, the more completely is the oxide thrown down; it combines, however, with a small portion of the acid; and as the resulting basic salt is, for the most part, slightly soluble in water, the quantity of the precipitate is decreased by too large an excess of water. —Ammonia precipitates the oxide completely, in bulky white flakes, which become dense after a while, and are not soluble in excess of the precipitant.—Potash produces the same flocculent precipitate, which, however, on the addition of a slight excess of potash, forms crystalline grains of a compound of antimonic oxide and potash on the sides of the vessel, and with a larger excess dissolves entirely.—Carbonate of ammonia, potash, or soda, and likewise the bicarbonates of these bases, completely precipitate the oxide in voluminous flakes, which gradually increase in density; they are slightly soluble in excess of the monocarbonate of potash only; the precipitation is attended with evolution of carbonic acid. (H. Rose.)—The carbonates of baryta, lime, and magnesia also precipitate antimonic oxide at ordinary temperatures. (Demarçay.)—Phosphate of soda precipitates white flakes, but leaves part of the oxide in solution. (H. Rose.) —Oxalic acid produces a very bulky precipitate, and after long standing, separates the whole of the oxide; with an excess of oxalic acid, the precipitate does not appear till after some time, but on longer standing the separation is likewise complete. (H. Rose.)—Ferrocyanide of potassium gives a white precipitate, insoluble in hydrochloric acid; tincture of galls, a yellowish-white precipitate. Ferricyanide of potassium does not affect the salts of antimonic oxide.—All antimonic salts which are insoluble in water, dissolve in hydrochloric acid, and then give the same reactions.

c. With Alkalis—*d.* with Sulphide of Antimony.

C. ANTIMONIOUS ACID. SbO^4.

Antimonige Säure, Acide antimonieux, Deutoxyde d'Antimoine.

Formation.—1. When antimony or sulphide of antimony is heated for some time in contact with the air; also when antimonic oxide is heated in the air. According to Berzelius, antimonic oxide, when finely divided, burns like tinder, till it is converted into antimonious acid. (Berzelius.)—2. When antimony is fused with sulphate of potash, antimonite of potash, sulphide of antimony, and sulphide of potassium are formed. (Liebig.)—3. By igniting antimonic acid. (Berzelius.)

Preparation.—1. By roasting sulphide of antimony as completely as possible. (Antimony-ash, *Spiessglanzasche.*)—2. By igniting antimonic acid or nitrate of antimonic oxide.

Properties.—White powder, which turns yellow every time it is heated; emits a vivid light in the blowpipe flame without fusing, and in the inner flame is slowly dissipated, but is otherwise fixed in the fire. (Berzelius.) Sp. gr. = 6·6952 (Karsten). Reddens litmus-paper when moistened. (H. Rose.)

	Calculation.		Berzelius. (1)	Berzelius. (2)	Thomson.	Thénard.	Proust.
Sb	129	80·12	78·2	80·127	80·84	80	77
4O	32	19·88	21·8	19·873	19·16	20	23
SbO^4	161	100·00	100·0	100·000	100·00	100	100

Or:

SbO^3	153	47·52
SbO^5	169	52·48
SbO^3, SbO^5	322	100·00

($Sb^2O^4 = 2 \,.\, 806{\cdot}45 + 4 \,.\, 100 = 2012{\cdot}9$. Berzelius.)

It may also be regarded as antimoniate of antimonic oxide$=SbO^3, SbO^5$. When antimonious acid is fused with excess of carbonate of soda, boiling water, if added in large quantity, chiefly dissolves out from the mass, a compound of antimonic oxide and soda, together with a small quantity of antimoniate of soda, leaving antimoniate of soda with a small quantity of the compound of antimonic oxide and soda undissolved. (Mitscherlich, *J. pr. Chem.* 19, 457.)

Decompositions.—When gently heated with potassium or sodium, antimonious acid is reduced to the metallic state, with incandescence. (Gay-Lussac & Thénard.)—It is likewise reduced to the metallic state by ignition with charcoal.—On charcoal in the inner blowpipe-flame the reduction is very difficult, because the reduced antimony volatilizes, and covers the charcoal all round with freshly formed oxide: the addition of carbonate of soda is indispensable to the formation of metallic globules. (Berzelius.)—By cyanide of potassium at a low red heat, the products being antimony and cyanate of potash. (Liebig.) When a mixture of antimonious acid and finely divided antimony is heated to redness, antimonic oxide is produced. (Proust.) $3SbO^4 + Sb = 4SbO^3$.—When antimonious acid is gently heated with iodide of potassium, iodine is evolved, and a compound of antimonic oxide and potash is formed. (Capitaine.)—When heated with a small quantity of sulphur, it yields sulphurous acid and glass of antimony; a larger proportion of sulphur gives rise to the formation of sulphurous acid and sulphide of antimony. (Proust.) $SbO^4 + 5S = SbS^3 + 2SO^2$.—By fusion with a small quantity of sulphide of antimony, it yields antimonic oxide, with evolution of sulphurous acid; with a larger quantity of the sulphide, oxy-sulphide of antimony is formed: $9SbO^4 + SbS^3 = 10SbO^3 + 3SO^2$.—Antimonious acid is not affected by a cold solution of bihydrosulphate of potash; a boiling solution, on the contrary, dissolves it with disengagement of hydrosulphuric acid, and acids added to the solution, precipitate tetrasulphide of antimony. (Berzelius.)

Combinations.—*a.* With water.—*α.* HYDRATE OF ANTIMONIOUS ACID.—Prepared by decomposing an aqueous solution of antimonite of potash or soda by an acid.—White flakes, which are insoluble in water, but redden litmus paper, even after the most prolonged washing with water. When heated, it gives off 5·26 per cent. of water, free from acid. (Berzelius.)

	Calculation.		Berzelius.
SbO^4	161	94·71	94·74
HO	9	5·29	5·26
HO, SbO^4	170	100·00	100·00

β. *Solution of Antimonious Acid.*—The acid dissolves in boiling water somewhat more readily than antimonic oxide; hydrosulphuric acid colours the solution yellow, but the colour disappears on the addition of ammonia. (Capitaine.)

b. Antimonious acid is sparingly dissolved by a few acids; hydrosulphuric acid added to these solutions, throws down an orange-yellow precipitate.

c. With Salifiable Bases, it forms salts called ANTIMONITES. When ignited with alkaline carbonates it expels the carbonic acid. The alkaline antimonites are colourless; they are decomposed by nitric and other acids, which remove the base and leave the antimonious acid undissolved. The latter is not perceptibly dissolved by the excess of acid; the precipitate is coloured orange-yellow by hydrosulphuric acid, and, when digested with iron and hydrochloric acid, deposits antimony in the form of a black powder. Some antimonites, when strongly heated become incandescent (I. 107), after which they are scarcely decomposed by acids. (Berzelius.) The alkaline antimonites do not exhibit this incandescence; they are decomposed by nitric acid even after ignition. If antimonious acid is regarded as antimoniate of antimonic oxide, its salts must consist of an antimoniate mixed with a compound of antimonic oxide and the same base.

D. ANTIMONIC ACID. SbO^5.

Antimonsäure, Acide Antimonique, Tritoxyde d'Antimoine.

Antimony-ochre appears sometimes to contain hydrate of antimonious acid, and sometimes hydrate of antimonic acid.

Formation.—1. By heating the metal or one of its lower oxides with nitric acid. According to Bourson (*Ann. Chim. Phys.* 70, 110; also *J. pr. Chem.* 17, 238), finely divided antimony, as it is obtained by precipitation with zinc, is completely converted into antimonic acid by digestion with nitric acid, either cold or hot, concentrated or dilute; and the resulting antimonic acid, after washing, evolves oxygen gas on ignition, without any admixture of nitrous acid. According to H. Rose, though the antimony in this state is strongly attacked by nitric acid, only a portion of it is converted into antimonic acid, even by boiling; and the nitrate of antimonic oxide formed at the same time is completely changed into antimonic acid, only by repeated evaporation to dryness with fresh quantities of nitric acid.—2. By deflagrating antimony with nitre.—3. By heating it with red oxide of mercury.

Preparation.—1. Antimonic acid is prepared by evaporating a solution of antimony in aqua-regia to dryness, treating the residue with strong nitric acid, and heating the mixture till the whole of the nitric acid is expelled, but not to redness. (Berzelius.) The *Bezoardicum minerale* was formerly prepared by mixing butter of antimony with strong nitric acid, evaporating, and repeatedly distilling off the nitric acid.—2. Powdered antimony is boiled with nitric acid, and the residue—which consists of hydrated antimonic acid and basic nitrate of antimonic oxide—is heated nearly to redness. (Berzelius.)—3. Powdered antimony is heated with red oxide of mercury till the green antimoniate of mercuric oxide, which is formed at first with emission of light and heat, is converted into yellow antimonic acid. (Berzelius.)—4. Hydrate of antimonic acid is heated not quite to redness. (Berzelius.)

Properties.—Pale lemon-yellow substance, which becomes darker every time it is heated. Tasteless. (Berzelius.) Reddens moistened litmus paper. (H. Rose.) Sp. gr. = 6·525. (Boullay.)

	Calculation.		Berzelius. (1)	Berzelius. (2)	Proust.	Thénard.	Thomson.
Sb	129	76·33	72·9	76·34	77	68	73·33
5O	40	23·67	27·1	23·66	23	32	26·67
SbO^5	169	100·00	100·0	100·00	100	100	100·00

(Sb^2O^5 = 2 . 806·45 + 5 . 100 = 2112·9. Berzelius.)

Decompositions.—Antimonic acid is resolved at a red heat into oxygen gas and antimonious acid. (Berzelius.) When heated with a small quantity of sulphur, it yields sulphurous acid and antimonic oxide; with more sulphur, the products are sulphurous acid and sulphide of antimony.

$$SbO^5 + S = SbO^3 + SO^2;$$

$$\text{and:} \quad 2SbO^5 + 11S = 2SbS^3 + 5SO^2.$$

By ignition with sulphide of lead, copper, or silver, it likewise disengages sulphurous acid and is converted into antimonic oxide. (Rammelsberg, *Pogg.* 52, 241.) With alkaline bihydrosulphates, it behaves like antimonious acid. (Berzelius.)

Combinations.—*a.* With Water.—*α.* HYDRATE OF ANTIMONIC ACID.—*Materia perlata Kerkringii, Magisterium Antimonii diaphoretici, Sulphur fixatum Stibii.*—1. A mixture of 1 part of antimony (or sulphide of antimony) and 4 parts of nitre is projected by small portions at a time into a red-hot crucible; the heat raised after the deflagration has ceased; the pounded mass exhausted with water; the filtrate, which contains antimoniate of potash, treated with excess of nitric acid; and the precipitated hydrate thrown on a filter and thoroughly washed with water. (Berzelius.) The biantimoniate of potash, which forms the residue after exhaustion with water, may likewise be converted into hydrate of antimonic acid, by boiling with dilute nitric acid and washing with water.—2. Pentachloride of antimony is decomposed by water and the precipitated hydrate washed with water. After the hydrochloric acid solution is washed away, the hydrate diffuses itself through the wash-water in so finely divided a state, that it passes through the filter and renders the liquid opalescent.

¶ The acid obtained by the second method, or in combination, by fusing ordinary antimoniate of potash with excess of alkali, is regarded by Fremy as a modification of antimonic acid, and distinguished by the name of *Meta-antimonic acid.* Meta-antimonic acid is bibasic, and dissolves slowly in ammonia, whereas the ordinary variety is quite insoluble in that menstruum; it likewise dissolves more easily in acids, and is perfectly soluble in a large quantity of water, from which it is again precipitated by acids. But from the facility with which it passes into the ordinary variety, there is great difficulty in accurately distinguishing the two acids. (E. Fremy, *Ann. Chim. Phys.* 3, 23, 407.) ¶

Fine white powder, which reddens litmus, and is insoluble in water: it gives off its water below a red heat. (Berzelius.)

	Calculation.		Berzelius.
SbO^5	169	94·94	94·91
HO	9	5·06	5·09
HO,SbO^5	178	100·00	100·00

¶ According to Fremy, the hydrate of the ordinary acid contains 21·7 per cent. of water (calculated 21·0) which gives the formula SbO^5+5HO; and the hydrate of meta-antimonic acid, 17·1 (calculated 17·5) per cent. corresponding to the formula SbO^5+4HO. ¶

β. Solution of Antimonic Acid.—The hydrate dissolves sparingly in water, forming a solution which behaves with hydrosulphuric acid like the solution of antimonious acid. (Capitaine.)

b. Antimonic acid is slightly soluble in hydrochloric and tartaric acid.

c. With Salifiable Bases, antimonic acid forms salts called ANTIMONIATES. From the alkaline carbonates it expels carbonic acid on ignition, but not from their boiling aqueous solutions. Through the researches of Berzelius, we are acquainted with compounds of 1 atom of base with 1 and with 2 atoms of antimonic acid; besides these, according to Fremy (*Compt. rend.* 16, 187), there exist salts which contain 1 atom of acid to 1½ and to 2 atoms of base, and are formed by igniting alkaline mono-antimoniates with excess of alkali. The antimoniates of the alkalis and earths are colourless. Only those of the more soluble alkalis are soluble in water. The antimoniates are decomposed even by weak acids. In these decompositions, the stronger acids, such as sulphuric or nitric acid, separate hydrate of antimonic oxide; carbonic acid, on the contrary, throws down a bi-antimoniate from a solution of the monobasic salt. The hydrate of antimonic acid thus precipitated is dissolved by excess of hydrochloric or tartaric acid on the application of heat, but not by any of the other acids; when digested with hydrochloric acid and iron, it yields a dark-coloured, easily fusible precipitate of metallic antimony, and turns orange-yellow when treated with hydrosulphuric acid. Strong hydrochloric acid dissolves most of the antimoniates. From the solution, zinc precipitates a black powder, consisting of metallic antimony; hydrosulphuric acid throws down an orange-yellow precipitate (provided the base does not also form a precipitate of a peculiar colour) easily soluble in hydrosulphate of ammonia. From the compounds of antimonic acid with the heavy metallic oxides, bihydrosulphate of ammonia withdraws the antimonic acid, and the filtrate, when treated with an acid, yields pentasulphide of antimony. Many antimoniates, especially those of zinc, cobalt, and copper, after all their water has been driven off at a red-heat, become incandescent without further loss of weight; they then assume a much lighter colour, and are afterwards but slightly, if at all, decomposed by acids. (Berzelius.)

ANTIMONY AND HYDROGEN.

A. *Solid Antimonide of Hydrogen?*—When antimony is made to conduct the negative electricity of a voltaic battery into water, a brownish-black substance is slowly formed. (Ruhland, *Schw.* 15, 480.)

B. ANTIMONIURETTED HYDROGEN GAS.—Discovered by L. Thomson.—*Formation.* 1. This gas is evolved on dissolving antimonide of zinc in dilute acids.—2. When zinc mixed with antimonic oxide, antimonious acid, or antimonic acid is dissolved in dilute acids. (Thomson.) Under these circumstances, a small portion only of the antimony passes off in the form of antimoniuretted hydrogen, the greater part remaining behind in the liquid, in the form of black pulverulent metallic antimony. (Jacquelain, *Compt. rend.* 16, 31.) If iron is substituted for the zinc, the hydrogen evolved is free from antimony. (Dupasquier, *Compt. rend.* 14, 514.) Antimonide of potassium likewise evolves pure hydrogen gas when put into water. (Capitaine.)

Preparation.—1. By dissolving an alloy of zinc and antimony in dilute sulphuric or hydrochloric acid. Thompson melts together equal parts of zinc and antimony, and thereby forms an alloy which, when treated with dilute sulphuric acid, yields a pure gas, unmixed with free hydrogen.—Lassaigne fuses 3 parts of zinc with 2 parts of antimony, and obtains a gas containing not more than 2 per cent. of free hydrogen. Capitaine treats a mixture of 2 parts of zinc and 1 part of antimony with dilute sulphuric acid, in which antimonic oxide is diffused. A. Vogel treats the same alloy with hydrochloric acid, and obtains a gas mixed with a large quantity of free hydrogen.—With equal parts of zinc and antimony, the evolution of gas proceeds slowly, but the gas is nearly pure. (Capitaine.)—With 2 parts of zinc to 3 parts of antimony, the evolution of gas is very feeble, and soon ceases altogether. (Lassaigne.)—2. By dissolving zinc in dilute sulphuric or hydrochloric acid, with which antimonic oxide, hydrochlorate of antimonic oxide, tartar-emetic, or *antimonium diaphoreticum* is mixed. (Thomson, A. Vogel.)

The pure gas is completely decomposed and absorbed by an aqueous solution of nitrate of silver; any free hydrogen that may be mixed with it, remains unaltered. (Lassaigne.)

Properties.—Colourless; has a peculiar odour; smells like arseniuretted hydrogen (Thomson); has a peculiar odour, but not like garlic (Pfaff); has a nauseating odour, somewhat like that of hydrosulphuric acid, but does not affect lead-salts. (Lassaigne.) It is inodorous. (Capitaine.)

	Calculation.		Lassaigne.
Sb	129	97·73	97·58
3H	3	2·27	2·42
SbH^3	132	100·00	100·00

Lassaigne decomposed the gas with nitrate of silver, and from the proportion of the antimony to the silver in the resulting precipitate, calculated the proportion of the antimony to the hydrogen in the gas.

Decompositions.—1. At a temperature below redness, the gas is resolved into antimony which is deposited in the form of a tin-white, metallic globule, and hydrogen which escapes as gas. (Thomson.)—The decomposition is affected even at a much lower temperature than that of arseniuretted hydrogen. (Simon.) The decomposition is not attended with perceptible diminution of volume. [?] (Lassaigne.) If the gas is decomposed by passing it through a hot tube, and iodine is then allowed to volatilize in the tube, the iodine forms with the metallic film a reddish-yellow amorphous mass insoluble in water (whereas arsenic would produce a brilliant, straw-coloured, crystalline compound, soluble in water). (Meissner & Hankel, *J. pr. Chem.* 25, 243; see also pp. 269, 270.)—2. When mixed with oxygen gas or atmospheric air, it explodes violently by the electric spark. (Thomson.)—When antimoniuretted hydrogen contained in a glass jar, is set on fire in contact with air, white flakes of antimonic oxide are deposited, but no metallic antimony (a character which serves to distinguish it from arseniuretted hydrogen). (A. Vogel, L. A. Buchner.) If a stream of the gas passing through a fine opening in a glass-tube be inflamed, it burns with a pale bluish-green light, producing dense white clouds of antimonic oxide, which forms a crystalline sublimate. Glass or porcelain if held in the flame, becomes covered with a metallic film similar to that obtained with arseniuretted hydrogen. (Thomson.) The film is black in the centre, and grey on the circumference; but if the tube is heated to redness at a distance of some inches from the exit of the gas, the film acquires a bright metallic lustre. (Pfaff.) In general, the antimony spots are darker than those of arsenic, and appear brown only when the antimony is in very small quantity; when the gas contains both antimony and arsenic, the metallic film appears black in the centre from the more fixed antimony, and brown on the circumference from the more volatile arsenic. An alloy of 5,000 parts of zinc to 1 part of antimony, yields, when dissolved in dilute sulphuric acid, a gas which gives well marked spots; with 11,000 parts of zinc, a few distinct spots are still obtained; and with 13,000 parts of zinc, (which is the limit,) only faint spots. If 0·0156 of a grain of tartar-emetic be added to a mixture of zinc and sulphuric acid, distinct spots of metal are deposited; with 0·01044 of a grain, less distinct, and with 0·00522 of a grain, (the limit,) only two or three very small spots. (Brett, *Phil. Mag. J.* 21, 405.)—3. When antimoniuretted hydrogen is kept for several days, it deposits antimony on the sides of the vessel, and in the water in which the receiver stands. This is more especially the case with gas which has been slowly disengaged; when rapidly evolved, it deposits thin flakes of antimony, even on the neck of the bottle in which it is generated. (A. Vogel.) The water round the receiver becomes blackened by the precipitated antimony. The larger the quantity of free hydrogen present in the gas, the more slowly does this decomposition take place. (Pfaff.) The decomposition is greatly accelerated by exposure to the sun's rays; it is not attended with perceptible change of volume. (Lassaigne.) This decomposition is due either to a slow combustion, possibly caused by the presence of a small quantity of air, or it is connected with the cause first described, viz. rise of temperature.

4. Chlorine, at ordinary temperatures, acts but slowly on antimoniuretted-hydrogen, forming a small quantity of chloride of antimony [and hydrochloric acid], but without any separation of metallic antimony; this change takes place even when the quantity of chlorine is very small. (A. Vogel, L. A. Buchner.) The mixture explodes by the electric spark. (Thomson.) On passing the gas through chlorine-water, nearly all the antimony is absorbed, aqueous hydrochloric acid and white flakes of oxy-chloride of antimony being formed. (Simon.)—5. An aqueous solution of bromine acts in a similar manner, retaining the whole of the antimony, and depositing white flakes, but without losing its own colour. (Simon.)—6. Aqueous solution of iodine retains the greater part of the antimony, becoming colourless, and depositing white flakes, which, if the stream of gas be continued, become first brown and then black, and are converted into metallic antimony; the supernatant liquid does not contain a trace of antimony. (Simon.)

7. The gas is slightly decomposed by an aqueous solution of sulphate of copper, but only when passed through it for a long time; a few black flakes of antimonide of copper being deposited. (Simon.)—8. An aqueous solution of nitrate of silver precipitates the whole of the antimony, in the form of a black powder of antimonide of silver. (Simon.) Probably thus:—

$$3(AgO, NO^5) + SbH^3 = Ag^3Sb + 3NO^5 + 3HO.$$

When the gas likewise contains arseniuretted hydrogen, the arsenic remains in the liquid as arsenious acid. (Simon.)—9. When the gas is slowly passed through an aqueous solution of protochloride of mercury, the whole of the antimony is separated, and the liquid becomes turbid, and deposits white flakes, which first turn grey and afterwards black. (Simon.) The grey precipitate when heated, yields a sublimate of dichloride of mercury, and leaves a yellow fused mass of antimonious acid, [antimonic oxide?] When heated with nitric acid, it is converted into dichloride of mercury, while the acid dissolves antimony. (Simon.) Probably a mixture of dichloride of mercury and oxy-chloride of antimony is first formed:—

$$12HgCl + SbH^3 = 6Hg^2Cl + SbCl^3 + 3HCl.$$

the $SbCl^3$ thus produced, is resolved by the water into hydrochloric acid and oxy-chloride of antimony;—with a larger proportion of the gas, whereby the precipitate is rendered darker, a mixture of dichloride of mercury and metallic antimony is probably formed:

$$6HgCl + SbH^3 = 3Hg^2Cl + Sb + 3HCl;$$

and the black precipitate is probably Hg^3Sb, thus:

$$3HgCl + SbH^3 = Hg^3Sb + 3HCl.$$

—10. The gas is decomposed by a solution of chloride of gold. (Jacquelain, *Compt. rend.* 16, 31.)—With an aqueous solution of bichloride of platinum, it rapidly forms a black precipitate of antimonide of platinum, the whole of the antimony being separated. (Simon.)

11. When passed through an alcoholic solution of potash or soda, it imparts a brownish-yellow, and then a dark-brown colour to the liquid, and, lastly, renders it turbid, and separates brownish-black flakes; an alcoholic solution of ammonia behaves similarly, but the turbidity is more slowly produced.—Arseniuretted hydrogen gas does not act on alcoholic solutions of the alkalis; but a gaseous mixture evolved from zinc, sulphuric acid, arsenious acid, and tartar-emetic, in which 10,000 parts of arsenious acid are mixed with 1 part of emetic-tartar, still imparts a brown colour to alcoholic solutions of the alkalis, and, with 100,000 parts of arsenious acid to 1 of tartar-emetic, a yellow colour. (Meissner & Hankel, *J. pr. Chem.* 25, 243.)—The following substances exert no decomposing action on antimoniuretted hydrogen gas; viz., strong sulphuric acid, hydrosulphuric acid, ammonia, potash, arsenious acid mixed with water, acetate of lead, sulphate of zinc, and protochloride of iron. (Simon.)

The gas is not sensibly absorbed by water. (Simon.)

Antimonic oxide does not combine with *Carbonic acid.*

ANTIMONY AND PHOSPHORUS.

A. PHOSPHIDE OF ANTIMONY.—1. Prepared by fusing antimony with an equal weight of glacial phosphoric acid, and with or without $\frac{1}{16}$ of its weight of charcoal powder.—2. By throwing pieces of phosphorus on fused antimony. White, brittle substance, having the metallic lustre and a laminated fracture; when thrown on red-hot charcoal, it burns with a small greenish flame. (Pelletier.)—When prepared by the second method, it has a fine-grained fracture, appears somewhat bluer than antimony itself, and when heated on charcoal before the blowpipe, does not exhibit the green flame; contains 15·46 per cent. of phosphorus. (Landgrebe, *Schw.* 53, 469.)

B. Phosphite of Antimonic Oxide.—When terchloride of phosphorus, dissolved in water and neutralized with ammonia, is mixed with tartar-emetic, and then with hydrochloric acid, a precipitate is obtained, which is white—evolves hydrogen gas free from phosphorus, on being ignited after drying—and is soluble in excess of hydrochloric acid. (H. Rose, *Pogg.* 9, 45.)

C. Phosphate of Antimonic Oxide.—Aqueous phosphoric acid dissolves a small quantity of antimonic oxide; the solution does not crystallize, but yields on evaporation, a blackish green mass, which fuses in a strong fire, forming a transparent glass. (Wenzel.)—From the acid solution, Brandes (*Schw.* 62, 201), obtained small prisms *c*, which, when washed with cold water, left *b*, and after several hours' washing with boiling water, the salt *a*.

		a.	Brandes.
$4SbO^3$	612·0	89·55	89·40
PO^5	71·4	10·45	10·31
$4SbO^3,PO^5$	683·4	100·00	99·71

		b.	Brandes.
$2SbO^3$	306·0	81·08	80·40
PO^5	71·4	18·92	19·55
$2SbO^3,PO^5$	377·4	100·00	99·95

		c.	Brandes.
$2SbO^3$	306·0	56·86	56·00
$3PO^5$	214·2	39·80	40·65
$2HO$	18·0	3·34	4·00
$2SbO^3,3PO^5 + 2Aq.$	538·2	100·00	100·65

¶ D. Pyrophosphate of Antimonic Oxide.—When antimonic oxide is boiled with solution of pyrophosphate of soda, a liquid is obtained, which holds a large quantity of the oxide in solution, and, when evaporated over oil of vitriol, forms a cauliflower-like mass. On digesting this mass with water, the greater part of the antimonic oxide is left undissolved. (Schwarzenberg, *Ann. Pharm.* 65, 2.) ¶

Antimony and Sulphur.

The compound SbS^2 (the existence of which was suspected by Faraday, *Pogg.* 23, 314), does not appear to exist. When an intimate mixture of 1 atom of antimony and 2 atoms of tersulphide of antimony is fused out of contact of air, and then slowly cooled, a quantity of the metal separates, amounting to 63 per cent. of that which was added to the sulphur compound. The superposed sulphide of antimony consists of a mixture of tersulphide of antimony and metallic antimony in feathery crystals; the latter remains behind on dissolving the tersulphide in hydrochloric acid. From this it appears, that tersulphide of antimony is capable of dissolving a small quantity of metallic antimony at its fusing point, but deposits it again on cooling. (Berzelius, *Pogg.* 37, 163.)

A. TERSULPHIDE OF ANTIMONY, ANTIMONIOUS SULPHIDE, SULPHANTIMONIOUS ACID. — *a. Crystallized.* — *Grey Sulphide of Antimony, Spiessglanz, roher Spiessglanz, Antimonium crudum.* — Found native in large quantity as *Grey Antimony ore,* which frequently also contains arsenic, lead, iron, and copper. On the large scale it is separated from the gangue by fusion. It is readily formed by fusing a mixture of its elements, or by fusing one of the oxides of antimony with excess of sulphur; the combination is attended with slight incandescence.

The presence of lead, iron, and copper is detected in sulphide of antimony in the same manner as in the regulus. To discover sulphide of arsenic, Liebig boils the finely powdered sulphide of antimony repeatedly with strong hydrochloric acid, till no more hydrosulphuric acid is disengaged; washes the residue, which contains the sulphide of arsenic, with water holding tartaric acid in solution; mixes it with carbonate of soda; and ignites it in a current of hydrogen gas, to sublime the arsenic (p. 274). Since finely divided sulphide of antimony is likewise slightly soluble in ammonia, we must not assume that sulphide of arsenic is present, merely because, after a few days' digestion with ammonia, the resulting liquid gives a yellowish-red precipitate with hydrochloric acid. In this case, the ammoniacal solution should first be exposed to the air for a few days till it ceases to become turbid from separation of antimonic oxide. After this, hydrochloric acid precipitates any arsenic that may be present, in the form of yellow sulphide of arsenic, which must then be more closely examined. If nothing more than a white cloudiness is produced by the hydrochloric acid, it arises merely from antimonic oxide still held in solution by the ammonia. (Garot, *N. J. Pharm.* 3, 118; also *J. pr. Chem.* 29, 83.)

To free commercial sulphide of antimony from sulphide of arsenic, it is digested in the levigated state with twice its weight of aqueous ammonia in a covered vessel, for 48 hours, the whole being frequently stirred; after which the residue is washed. The ammonia removes the sulphide of arsenic almost completely. (Weigand, *Centralblatt,* 1840, 175.) To obtain pure tersulphide of antimony, a finely powdered mixture of 13 parts of purified antimony and 5 parts of flowers of sulphur is projected by successive portions into a red-hot crucible, heated till it is perfectly fused, and then left to cool. When the antimony is not finely pulverized, part of it does not combine with the sulphur, but is deposited in the metallic state below the sulphide of antimony. (Liebig.)

Crystalline system of the native compound, the right prismatic: *Fig.* 44 (sometimes with the *t*-face), 70, and other forms. $a : a' = 107° 56'$; $a' : a$ behind $= 110° 58'$; $a : a'' = 109° 24'$; $a : u = 144° 42'$; $u : u' = 87° 54'$ (Hauy), 88° 40′ (Phillips), 89° 15′ (Mohs). Cleavage distinct parallel to *t*, less distinct parallel to *p*, *m*, and *u*. Artificially prepared sulphide of antimony has a radiated structure. Sp. gr. 4·620 (Mohs), 4·626 (Breithaupt); the tersulphide precipitated from the hydrochloric acid solution by hydrosulphuric acid, and then fused, has a specific gravity of 4·752. (Karsten.) Of the same degree of hardness as rock-salt; very brittle. Colour lead-grey; yields a blackish-grey powder. Easily fusible; on solidifying after fusion, it contracts strongly and becomes interspersed with cracks. At a strong red-heat, it boils and may be distilled without decomposition if the air be excluded.

	Calculation.		Berzelius.	Thomson.	Bergman.
Sb	129	72·88	72·8	73·77	74
3S	48	27·12	27·2	26·23	26
SbS^3	177	100·00	100·0	100·00	100

	J. Davy.	Vauquelin.	Proust.
Sb	74·16	75	75·1
3S	25·84	25	24·9
SbS^3	100·00	100	100·0

Decompositions.—1. When heated in the air not quite to its fusing point it consumes away, and at a higher temperature burns with a blue flame, yielding in both cases sulphurous acid gas and antimonious acid. The antimonious acid is mixed at first with antimonic oxide. According to Buchner (*Repert.* 13, 202), the powder is oxidized slowly in the air at ordinary temperatures, so that, after a while, cream of tartar dissolves out antimonic oxide from it. The grey antimony ore sometimes appears to be converted into the white variety. (Haidinger, *Pogg.* 11, 178.)—2. Hot nitric acid decomposes sulphide of antimony, yielding sulphur, sulphuric acid, and antimonic oxide, which remains in the form of a white powder mixed with the sulphur, in combination partly with sulphuric and partly with nitric acid. In a similar manner, dilute sulphuric acid mixed with nitre gradually produces, with the aid of heat, a mixture of sulphur and sulphate of antimonic oxide; and a mixture of hydrochloric acid with a moderate quantity of nitric acid forms a solution of terchloride of antimony, and separates sulphur.—3. Oil of vitriol boiled with tersulphide of antimony slowly produces a solution of acid sulphate of antimonic oxide, sulphurous acid being disengaged, and a fused mass of sulphur separated: the solution is decomposed by water.—4. When aqueous vapour is passed over ignited sulphide of antimony, a large quantity of hydrosulphuric acid and antimonic oxide is formed, the latter subliming in combination with undecomposed sulphide of antimony, in the form of an orange-yellow substance. (Regnault, *Ann. Chim. Phys.* 62, 383.)—5. Hydrochloric acid gas decomposes heated sulphide of antimony, yielding hydrosulphuric acid gas and terchloride of antimony ($SbS^3 + 3HCl = SbCl^3 + 3HS$); whereas, hot concentrated hydrochloric acid produces acid hydrochlorate of antimonic oxide, with evolution of hydrosulphuric acid gas.—6. Chlorine gas converts heated sulphide of antimony into chloride of sulphur and terchloride of antimony. (H. Rose.)—7. When hydrogen gas is passed over ignited sulphide of antimony, hydrosulphuric acid is formed and antimony reduced. (H. Rose, *Pogg.* 3, 443; Berthier.) Phosphuretted hydrogen gas in contact with ignited sulphide of antimony yields hydrosulphuric acid gas together with phosphorus and metallic antimony, which sublime. (H. Rose, *Pogg.* 20, 336.)—8. Charcoal decomposes tersulphide of antimony at a strong red heat, the products being bisulphide of carbon and metallic antimony. (Berthier, *Ann. Chim. Phys.* 22, 239.) By passing carbonic oxide gas over hot sulphide of antimony, the metal is imperfectly reduced. (Göbel, *J. pr. Chem.* 6, 388.)—9. Many metals, *e. g.* potassium, sodium, tin, iron, copper, &c. likewise separate the sulphur at a red heat; the reduced antimony combines with the excess of the other metal, and the new metallic sulphide sometimes unites with the undecomposed portion of sulphide of antimony. Metallic oxides mixed with charcoal act in a similar manner to the metals themselves, because the charcoal separates their oxygen.—10. A mixture of tersulphide of antimony and cyanide of potassium yields, at the fusing point, metallic antimony and sulphocyanide of potassium. (Liebig.)—11. When mixed with nitre, sulphide of antimony explodes at a red heat, yielding nitrate and antimoniate of potash.

12. When the fixed alkalis are ignited with tersulphide of antimony, they are decomposed, together with a portion of the tersulphide, forming antimonic oxide and a sulphide of the alkali-metal, by interchange of the oxygen and sulphur; the alkaline sulphide then combines with the sulphide of antimony, which remains undecomposed, producing a double sulphide of antimony and the alkali-metal; and the antimonic oxide formed combines either with undecomposed alkali when that substance is in excess, or with a portion of the tersulphide of antimony, when an excess of that compound has been used. (Berzelius.)—*a.* When carbonate of potash is ignited with excess of tersulphide of antimony (the carbonic acid, since it escapes, may be neglected), the whole of the potash and a portion of the sulphide of antimony are decomposed, yielding sulphide of potassium and antimonic oxide. Each of these compounds then takes up as large a portion of the excess of sulphide of antimony as it is capable of combining with, so that two layers are formed, the lower one of which contains the antimonic oxide combined with the sulphide of antimony, and the upper the sulphide of potassium combined with the same substance. (*Sch.* 60.)

$$3KO + SbS^3 + xSbS^3 + ySbS^3 = 3KS, xSbS^3 + SbO^3, ySbS^3.$$

—*b.* When, on the contrary, tersulphide of antimony is ignited with excess of carbonate of potash, 5 atoms of the sulphide do not expel more than 7 atoms of carbonic acid; and the rest of the carbonate of potash remains unaltered. The following reactions then take place: 6 atoms of potash and 2 atoms of tersulphide of antimony produce 6 atoms of sulphide of potassium and 2 atoms of antimonic oxide; the seventh atom of potash unites with the 2 atoms of antimonic oxide, and the 6 atoms of sulphide of potassium with 3 atoms of tersulphide of antimony. (*Sch.* 61.)

$$7KO + 5SbS^3 = 6KS, 3SbS^3 + KO, 2SbO^3.$$

(Berzelius.) By strongly igniting this mass in a close vessel, a small quantity of metallic antimony is reduced, because, according to Berzelius, the compound of antimonic oxide and potash is resolved into antimony and antimonite of potash: $2(KO, 2SbO^3) = 2KO, 3SbO^4 + Sb$; but according to H. Rose, because the compound of sulphide of potassium and tersulphide of antimony is converted into a compound of sulphide of potassium with pentasulphide of antimony,—somewhat in the following manner: $10KS + 5SbS^3 = 10KS + 3SbS^5 + 2Sb$.—By boiling tersulphide of antimony with aqueous potash, a solution is obtained which contains sulphide of potassium in combination with tersulphide of antimony, and a small quantity of the compound of antimonic oxide and potash, while a yellowish-brown mixture of the latter compound and oxy-sulphide of antimony (*Crocus antimonii*) is left behind. The reaction is the same in this case as in the dry way, if we assume that the metallic sulphides dissolve in water without change of composition: $3KO + SbS^3$ yield $3KS$ and SbO^3; the $3KS$ then dissolves a quantity of the undecomposed SbS^3, increasing with the temperature of the liquid; and the SbO^3 produced combines partly with potash, forming a compound which remains for the most part undissolved, and partly with the excess of sulphide of antimony. If, however, we suppose that the metallic sulphides dissolve as hydrosulphates of the metallic oxides, then the reaction will be as follows: $3KO + SbS^3 + 3HO = 3(KO,HS) + SbO^3$;

the 3(KO,HS) then dissolve a portion of the remaining SbS^3, which, by undergoing mutual decomposition with 3 atoms of water, is converted into $SbO^3,3HS$, so that a double hydrosulphate is produced $=(KO,HS)+x(SbO^3,3HS)$. The other changes are explained as in the first scheme. Boiling carbonate of potash or soda acts on sulphide of antimony in a similar manner, but much less strongly. Grey sulphide of antimony is but very sparingly soluble in aqueous ammonia. If one part of finely powdered sulphide of antimony is left in contact with 1000 parts of ammonia for some days, about half of it dissolves; the other portion remaining undissolved even when treated with fresh ammonia. The yellow solution gives a red precipitate with hydrochloric acid. (Garot.)

b. Amorphous Tersulphide of Antimony.—Brownish red Sulphide of Antimony, Mineral Kermes, Carthusian powder, Kermes Minerale, Pulvis Carthusianorum. —[The kermes which Becquerel obtained, apparently in octohedrons, by electrolysis (I. 394), deserves more precise examination.]—*Formation* and *Preparation.*—1. This substance is obtained by fusing grey sulphide of antimony in a thin glass vessel for a long time till it forms a perfectly uniform mass, and then throwing the whole as quickly as possible into cold water. (Fuchs, *Pogg.* 31, 578.) The shorter the time of fusion, and the slower the cooling, the larger is the quantity of crystallized sulphide of antimony mixed with the kermes.

2. Antimonic oxide is precipitated from its solutions in acids by hydrosulphuric acid.—*a.* By passing hydrosulphuric acid gas through the aqueous solution of tartar-emetic, as long as a precipitate is formed, and afterwards washing the precipitate continuously with hot water.—Since the precipitated kermes is mixed with cream of tartar, which is difficultly soluble, Schmidt (*Mag. Pharm.* 13, 56) decants the solution from the precipitate, adds water to the latter and enough carbonate of potash to render the liquid slightly alkaline—whereby the cream of tartar is converted into the easily soluble monotartrate of potash—and lastly washes the kermes on a filter.—*b.* By precipitating the clear solution of terchloride of antimony in aqueous tartaric acid with hydrosulphuric acid. At first, a reddish yellow compound of sulphide of antimony with a small quantity of the terchloride is precipitated; so that it is necessary to saturate the liquid completely with hydrosulphuric acid, and then to heat the mixture very gently for some time; after this, the kermes contains but a trace of terchloride of antimony. (H. Rose.)

3. Finely pounded grey sulphide of antimony is boiled for a long time with an aqueous solution of carbonate of potash or soda, the liquid filtered at a boiling heat, and then left to deposit the kermes on cooling. The alkaline solution filtered from the precipitated kermes, if boiled with the insoluble residue and filtered hot, again deposits kermes, and so on, several times.—This is the oldest method of preparing kermes, as practised by Glauber, Simon, and La Ligerie.—When the grey sulphide of antimony is boiled with a strong solution of carbonate of potash, carbonic acid is evolved; but with a dilute solution this is not the case (Duflos); neither is carbonic acid evolved when carbonate of soda is used,—an alkaline sesquicarbonate being probably formed. (Duflos, O. Henry, H. Rose.)—While the greater part of the alkaline carbonate remains unchanged, or becomes charged with more carbonic acid, a small portion of the alkali acts upon the sulphide of antimony, in such a manner as to produce antimonic oxide and a sulphide of the alkali-metal. The latter dissolves part of the remaining sulphide of antimony, the greater part of which separates in

the form of kermes on cooling. The antimonic oxide is contained in the liquid in combination with the alkali, but partly separates on cooling, combined with a small quantity of alkali and mixed with the kermes, in the form of acuminated six-sided needles, which may be detected by the microscope. Since, however, it does not separate so rapidly as the kermes, the latter may be obtained free from antimonic oxide, by collecting it on a filter immediately after its formation. Carbonate of potash precipitates a smaller quantity of antimonic oxide than carbonate of soda. The larger the excess of alkaline carbonate present, the smaller is the proportion of antimonic oxide thrown down. Thus, by boiling 1 part of grey sulphide of antimony with 1 part of crystallized carbonate of soda, only a small quantity of antimonic oxide is precipitated, and with still more carbonate of soda (which, however, gives but a scanty precipitate of kermes), the whole of the antimonic oxide remains dissolved, provided the kermes be rapidly collected on a filter. (H. Rose.) The solution filtered from the kermes contains—besides a large quantity of alkaline carbonate—more or less sulphide of potassium or sodium, still combined with a small proportion of sulphide of antimony, and accordingly, when treated with the stronger acids, it evolves carbonic acid and hydrosulphuric acid gas, and deposits a yellowish-red precipitate. (O. Henry, Liebig.) According to H. Rose, it does not give off hydrosulphuric acid gas, because it likewise contains antimonic oxide, in quantity more than sufficient to form sulphide of antimony with the hydrosulphuric acid separated from the sulphide of sodium. When grey sulphide of antimony is boiled with a dilute solution of carbonate of potash (which likewise does not evolve any carbonic acid gas), the solution filtered from the kermes does not give off hydrosulphuric acid on the addition of the stronger acids. (Duflos.)—The yellowish red precipitate produced by acids is kermes mixed, after a while, with pentasulphide of antimony: the longer the solution had previously been exposed to the air, the sooner does the precipitation of pentasulphide take place.

The residue obtained after exhausting grey sulphide of antimony with the boiling solution of an alkaline carbonate, consists of sulphide of antimony, antimonic oxide, and free alkali. (Duflos.)

When grey sulphide of antimony is boiled, for 10 minutes only, with carbonate of soda in a close vessel furnished with a gas-delivery tube, the filtrate yields a flocculent, greyish-brown kermes, which, when digested with a hot solution of tartaric acid, deepens in colour, and gives up a large quantity of antimonic oxide and soda—the latter being contained in the kermes in the form of sulphide of antimony and sodium; the supernatant mother-liquid contains sulphide of sodium. If, on the contrary, the mixture be boiled for an hour in an open vessel, a bright-coloured, pulverulent kermes is obtained, which gives up to acids a large quantity of antimonic oxide, and very little soda, and when decomposed by hydrogen gas yields 71·3....73·8 per cent. of antimony, with a small proportion of sulphide of sodium. (Liebig.)

The kermes 2, *b*, precipitated by hydrosulphuric acid, is not soluble in a cold solution of carbonate of soda; but in a hot solution, it dissolves much more abundantly than the grey sulphide of antimony, and evolves carbonic acid gas. The kermes which separates from the filtrate on cooling contains antimonic oxide, and the supernatant liquid contains sulphide of sodium. (Liebig.) In this case, a much larger quantity of antimonic oxide is deposited with the kermes than when the grey sulphide of antimony is used, because the solution contains a much smaller excess of carbonate of soda. (H. Rose.) When the boiling is continued for 10 minutes only, the resulting dingy coloured kermes behaves in a similar manner to that which is prepared from the grey sulphide by the same process, and the supernatant liquid holds in solution but a small quantity of antimonic oxide and sulphide of sodium. But if the boiling be continued for an hour, a more brilliant and finely divided kermes is precipitated, having the same properties as the kermes obtained by boiling grey sulphide of antimony for an hour, and the supernatant mother-liquid contains more sulphide of sodium, together with a small quantity of pentasulphide of antimony, produced by the action of the air during the prolonged ebullition. (Liebig.)

With 100 parts of grey sulphide of antimony, the following proportions of dry carbonate of potash and of water have been used; 25 parts of carbonate of potash to 200 parts of water. (*Paris Codex*, 1748.)—222: 1788; yields after boiling for a quarter of an hour, 18 parts of kermes free from oxide, the mother-liquid containing but a trace of sulphide of antimony; but after two hours' boiling the yield is only 13 parts of kermes free from oxide, and the mother-liquid contains more sulphide of antimony. (Duflos.)—400 : 1600; an old recipe of La Ligerie.—1600 : 4800; yields, after a quarter of an hour's boiling, 20 parts of pure kermes. (Duflos.)—By boiling 100 parts of sulphide of antimony with 200 parts of carbonate of potash and 1800 parts of water for two hours, and then precipitating the filtrate immediately with hydrochloric acid, 28 parts of kermes free from oxide are obtained. (Duflos.)

Cluzel boils 1 part of grey sulphide of antimony with 20 parts of crystallized carbonate of soda and 200 parts of water. The resulting kermes contains, according to Gay-Lussac, 30 per cent. of antimonic oxide. When the mixture is boiled for half an hour, it contains 18 per cent. of oxide, but in reality, the portions of kermes first precipitated contain only 14 per cent of oxide, while the subsequent portions are contaminated with nearly 29 per cent. (Duflos.)—A mixture of 100 parts of sulphide of antimony with 800 parts of crystallized carbonate of soda and 2400 parts of water boiled for half an hour, deposits 8 parts of kermes containing more than 1 part of antimonic oxide; by again boiling the mother-liquid with the residue, 9 parts of kermes are obtained, contaminated with 1·5 parts of oxide. (Duflos.)

Carbonate of potash produces a larger quantity of kermes than carbonate of soda (O. Henry); but the kermes prepared with carbonate of soda has a finer red colour. (Cluzel.)

As the grey sulphide of antimony is difficultly soluble in carbonate of soda, the precipitated red sulphide is preferable for this process. One part of finely powdered grey sulphide should therefore be boiled with 1 part of hydrate of potash and 30 parts of water for one hour; the filtrate precipitated while still hot by dilute sulphuric acid; and the mixed salts divided into three equal parts, each of which is then to be washed with water in a separate vessel, by subsidence and decantation, and afterwards collected on a filter. The precipitate collected on the first filter is then thrown by successive portions into a boiling filtered solution of 1 part of dry carbonate of soda in 34 parts of water, and the whole boiled for an hour; and the solution—which need not be filtered, since nothing remains undissolved—is then slowly cooled to separate the kermes. The solution poured off from the precipitated kermes is again raised to the boiling point, and the contents of the second filter added to it, and similarly with the third filter. The kermes deposited after the second boiling has usually the finest colour. The kermes thus prepared amounts, after washing with cold water and drying, to half the quantity of the grey sulphide used. It must be regarded as $SbO^3,2SbS^3$ (a composition similar to that of red antimony ore), but it still contains between 1 and $1\frac{1}{2}$ per cent. of soda. (Liebig, *Handwörterb.* 1, 427.)

4. Grey sulphide of antimony is boiled with solution of potash, not in excess, and the liquid filtered hot and then left to cool. The solution filtered from the precipitated kermes, if boiled afresh with the undissolved residue, yields a small additional quantity of kermes. Caustic potash dissolves sulphide of antimony much more abundantly than the carbonate; in other respects, the process is mainly the same. Thus $3KO$ is resolved with SbS^3 into $3KS$ and SbO^3; the $3KS$ then dissolves a certain quantity of the remaining SbS^3, a portion of which separates on cooling in the form of kermes. The SbO^3 thus formed remains partly dissolved in the alkaline solution, and partly, together with potash, combines with the SbS^3 which remains undissolved, thereby converting it into a yellow or brown crocus, from which, after a while, the liquid filtered from the kermes is unable to abstract any more SbS^3. According to Rose, however, the kermes thus obtained differs from that prepared with alkaline carbonates. It is not precipitated in the state of powder, but forms a dark brown jelly on cooling; it is difficult to wash and dry, and in drying shrinks up to a hard dark-brown mass having a conchoidal fracture. It does not contain antimonic oxide, but is in reality a feeble compound of tersulphide of antimony with a small quantity of sulphantimoniate of potassium. After washing for a short time, its composition is $2SbS^3+KS,SbS^5$; after longer washing with hot water, $9SbS^3+KS,SbS^5$. The formation of the KS,SbS^5 is to be attributed either to the partial resolution of the SbS^3 by boiling into metallic antimony and SbS^5, or—as Rose considers more probable—to the action of the air, whereby a portion of the antimony is oxidized and the proportion of the sulphur to the antimony increased. Hence kermes of this kind does not yield antimonic oxide when digested with a boiling solution of cream of tartar, but merely gives off a small quantity of hydrosulphuric acid gas; with dilute hydrochloric acid it evolves hydrosulphuric acid gas in abundance; and on ignition in a current of hydrogen, it yields water (previously contained in the KS,SbS^5 as water of crystallization) and metallic antimony, surrounded however by fused KS,SbS^5. (H. Rose.)

When grey sulphide of antimony is boiled with excess of potash, the filtrate does not deposit kermes on cooling. (Duflos, H. Rose.) But if carbonic acid gas be passed through the solution, a brilliant kermes is precipitated in large quantity; and when the carbonic acid ceases to cause any further precipitation, the stronger acids, after expelling the carbonic acid, throw down pentasulphide of antimony from the liquid filtered from the kermes. Moreover, if the liquid precipitated by carbonic acid and filtered from the kermes be boiled with a fresh quantity of sulphide of antimony, it deposits kermes on cooling, because the solution then contains carbonate of potash; on again passing carbonic acid through the liquid, no further precipitate is formed. (Hennsman, *Taschenb.* 1822, 184.) [The carbonic acid precipitates not only the tersulphide but also the pentasulphide of antimony.] The above solution, if treated with bicarbonate of potash or soda, instead of carbonic acid, likewise deposits a large quantity of kermes which is free from antimonic oxide, but on being treated with dilute hydrochloric acid, deepens in colour and gives up a small portion of potash; when reduced by hydrogen gas, it leaves antimony together with a double sulphide of antimony and potassium. (Liebig.)

If 100 parts of grey sulphide of antimony are boiled for a quarter of an hour with 30 pts. of hydrate of potash and 300 pts. of water, the filtrate deposits, on cooling, 25 pts. of kermes free from antimonic oxide; by boiling the residue a second time with the mother-liquid, 10 pts. of kermes are obtained; a third boiling yields 3·2 pts. The insoluble residue amounts to 49 pts. By boiling, for a quarter of an hour, a mixture of 100 parts of sulphide of antimony, 33 pts. of hydrate of potash, and 700 pts. of water, 13 pts. of kermes free from oxide are obtained; and by the second boiling, 10 pts.; after this, nothing more is deposited. The mother-liquid yields, on the addition of sulphuric acid, 18 pts. of brick-red kermes, containing but little pentasulphide of antimony, since it dissolves entirely in strong hydrochloric acid, with the exception of a small quantity of sulphur. A mixture of 100 pts. of sulphide of antimony and 60 pts. of hydrate of potash yields, after boiling with water a quarter of an hour, a filtrate which does not deposit any kermes on cooling. But by boiling 100 pts. of sulphide of antimony and 100 pts. of hydrate of potash with 2770 pts. of water for an hour and then filtering, a solution is obtained which deposits 9 parts of yellowish kermes containing a large quantity of antimonic oxide. The mother-liquid, if boiled three times with the residue, deposits a yellow powder—amounting to 6·3, 5·3, and 4 pts. —which becomes richer in oxide after each boiling, so that the powder obtained by a fourth boiling contains more than half its weight of antimonic oxide. When the mother-liquid from the kermes has been boiled with the insoluble residue till it no longer deposits kermes, it may again be made to yield that substance in abundance and free from impurity, by boiling it with fresh sulphide of antimony; and this process may be repeated several times. (Duflos.)

According to some formulæ, the potash-solution is boiled with sulphide of antimony and free sulphur. For instance: a mixture of 100 pts. of grey sulphide of antimony, 25 pts. of sulphur, 150 pts. of hydrate of potash, and 2400 pts. of water, boiled for half an hour and then filtered, deposits, on cooling, 33 pts. of fine brownish-red kermes free from antimonic oxide or excess of sulphur; and by boiling the mother-liquid a second time with the residue, the latter is entirely dissolved, and the solution yields, on cooling, a kermes nearly as pure and abundant as in the first case. The mother-liquid contains, not antimonic oxide, but hyposulphite of potash. With 100 pts. of sulphide of antimony, 50 pts. of sulphur, 150 pts. of hydrate of potash, and 4800 pts. of water, a mixture of kermes and sulphur is deposited; and with 100 pts. of sulphide of antimony, 100 pts. of sulphur, 300 pts. of hydrate of potash, and 4800 pts. of water, the filtrate deposits nothing on cooling, and only pentasulphide of antimony on the addition of acids. (Duflos.)

Kermes may also be prepared by the displacement method. Thus: coarsely pounded glass or quartz is placed at the bottom of a funnel, and upon it an intimate mixture of 1 pt. of very finely pulverized grey sulphide of antimony and 2 pts. of dry carbonate of soda (carbonate of potash, according to Boullay, produces a less brilliant kermes), 3 pts. of slaked lime, and 4 pts. of washed and dry sand; the mixture is covered with a layer of sand; and cold water allowed slowly to trickle upon it, as long as the liquid which passes through is precipitated by acids. The kermes is thrown down from the filtrate by a current of carbonic acid gas or by bicarbonate of soda. (Musculus, *J. Pharm.* 22, 241; also *Ann. Pharm.* 18, 344.)

According to Liebig, kermes free from antimonic oxide may be most conveniently prepared by the following process: a mixture of 1 pt. of finely pounded sulphide of antimony with 1 pt. of carbonate of potash, 1½ pt. of hydrate of potash, and 15 pts. of water is digested in a close vessel for two hours; the filtrate diluted with a large quantity of water, and precipitated by sulphuric acid; the precipitate boiled with dilute sulphuric acid—to decompose the sulphide of potassium mixed with the sulphide of antimony—and the residue washed with water.

5. Grey sulphide of antimony is fused with carbonate of potash or soda, and the mass, consisting of a mixture of sulphantimonite of potassium or sodium and the compound of antimonic oxide and potash or soda, is exhausted with water, filtered hot, and the solution left to cool. If 37·5 pts. (upwards of 7 At.) of carbonate of potash are used with 100 pts. (8 At.) of sulphide of antimony, the following decomposition takes place:

$$8SbS^3 + 7(KO, CO^2) = 6(KS, SbS^3) + KO, 2SbO^3 + 7CO^2.$$

The compound of antimonic oxide and potash is resolved by strong ignition into metallic antimony and antimonite of potash. Hot water dissolves out the sulphide of potassium, together with the greater part of the sulphide of antimony, which partially separates in the form of kermes as the filtrate cools; the insoluble residue contains sulphide of antimony, antimonic oxide, antimonious acid, and potash. (Berzelius.) The separation of metallic antimony after prolonged fusion is due to the formation, not of antimonite of potash, but of KS, SbS^5. (Duflos, H. Rose.) This decomposition is caused by the predisposing affinity of the sulphide of sodium for pentasulphide of antimony, because the pentasulphide is a stronger acid than the tersulphide. When the fused mass is thoroughly boiled with water, the double sulphide of antimony and potassium (or sodium) dissolves in the water; and moreover, antimonic oxide is dissolved by the undecomposed alkaline carbonate, and, on cooling, separates, together with the kermes, in fine needles, which are free or almost free from alkali. The quantity of kermes thus obtained is much greater than that which is produced by boiling grey sulphide of antimony with carbonate of soda, because more sulphide of antimony is decomposed by fusion; but the kermes has more of a yellowish-brown colour, and contains a larger quantity of antimonic oxide, though in variable proportions. The more rapidly the kermes is collected on the filter after cooling, the less is the quantity of oxide mixed with it. Besides antimonic oxide, it contains a compound of sulphide of potassium or sulphide of sodium with pentasulphide of antimony; hence a kermes prepared in this manner with carbonate of soda yields, when decomposed by chlorine gas, 8·5 per cent. of chloride of sodium. The liquid from which the kermes has been deposited on cooling in close vessels, contains carbonate of soda, sulphantimonite of sodium, and sulphantimoniate of sodium; so that on evaporation it yields, first crystals of sulphantimoniate of sodium and then of carbonate of soda; and, on the addition of bicarbonate of soda, deposits brownish-red kermes, in consequence of the decomposition of the sulphantimonite of sodium. (H. Rose.)

The larger the proportion of alkaline carbonate, and the longer the fusion is continued, the smaller is the quantity of antimonic oxide mixed with the kermes; but if too much alkaline carbonate is used, no kermes is deposited. (Duflos.) When a mixture of 100 pts. of grey sulphide of antimony with 37·5 pts. of carbonate of potash is heated merely to tranquil fusion, no metallic antimony is separated, but the resulting mass, after repeated exhaustion with water, yields 21 pts. of kermes, containing 25 per cent. of antimonic oxide. The same mixture if kept at a red heat for half an hour, deposits metallic antimony, and yields 19 pts. of kermes containing 9 per cent. of oxide. (Duflos.) Geiger obtained a good kermes, containing not more than 4 per cent. of oxide by the following process recommended by Berzelius:—100 pts. of sulphide of antimony heated to tranquil fusion with 50 pts. of carbonate of soda yield, on the first exhaustion with water, 17 pts. of kermes, containing 30 per cent. of antimonic oxide; on the second, 12·5 pts.; and on the third, 11 pts. The mother liquid contains antimonic oxide. (With these proportions, Pagenstecher obtained, by one exhaustion, 14 pts. of kermes containing 33 per cent. of oxide.) The same mixture kept at a red heat for half an hour, whereby a large quantity of metallic antimony is reduced, yields, in three exhaustions, 28, 19, and 17 pts. (together = 64 pts.) of kermes containing 9 per cent. of antimonic oxide. The mother-liquid contains antimonious acid. 100 pts. of sulphide of antimony fused for a short time with 67 pts. of carbonate of potash, yield, in one exhaustion with water, 10·3 pts. of kermes containing 21 per cent. of antimonic oxide; but after fusion for half an hour, whereby 8 pts. of metal are reduced, the same mixture yields 23 pts. of kermes containing 6·5 per cent. of oxide. When a mixture of 100 parts of sulphide of antimony and 150 pts. of carbonate of potash is fused for half an hour, 12·5 parts of metallic antimony are separated; but the solution, after exhausting with water, does not deposit any kermes on cooling; it contains antimonious acid, and, when treated with acids, deposits a mixture of kermes and pentasulphide of antimony. (Duflos.)

A mixture of 100 pts. of grey sulphide of antimony with 50 pts. of dry carbonate of soda, yields 9 pts. of kermes containing 42 per cent. of oxide; 100 sulphide of antimony and 100 carbonate of soda, yield 52 pts. of kermes containing 34 per cent. of oxide. (Pagenstecher.)

100 pts. of sulphide of antimony yield with 50 pts. of dry carbonate of soda a large quantity of kermes, rich in oxide, and resembling that obtained with carbonate of soda in the wet way. The mother-liquid gives with carbonate of ammonia a flame-coloured precipitate, and with bicarbonate of soda, a brownish-red bulky precipitate; both these precipitates are free from antimonic oxide, and dissolve perfectly in a hot solution of carbonate of soda; the solution deposits good kermes on cooling.—A mixture of 100 pts. of sulphide of antimony and 100 pts. of carbonate of soda fuses less readily, yields more metallic globules, and leaves a smaller residue when exhausted with water; nevertheless, the filtrate deposits a smaller quantity of kermes on cooling, and, therefore, gives a larger precipitate with alkaline bicarbonates.—With 100 pts. of sulphide of antimony to 200 pts. of carbonate of soda, a large quantity of metal is reduced, and the mass dissolves almost completely in hot water; nevertheless the filtrate, when cooled in close vessels, does not deposit any kermes, but, after a while, white crystalline flakes of antimonite of soda separate from it; bicarbonate of soda, however, throws down from the filtrate a considerable quantity of kermes free from antimonic oxide. Hence by using an excess of carbonate of soda, too large a quantity of sulphide of sodium is produced, whereby the whole of the sulphide of antimony is retained in solution. (Liebig.)

Liebig fuses a mixture of 100 pts. sulphide of antimony and 25 pts. dry carbonate of soda at a gentle heat, stirring all the while with a pipe-stem; then pours the mass out upon a brick; reduces it to fine powder; boils 1 pt. of the powder with 2 pts. of crystallized carbonate of soda and 16 pts. of water, for an hour; filters; sets the liquid aside to cool; decants the solution from the kermes; boils it with the undissolved residue; and so on repeatedly, till only yellow or yellowish-brown *Crocus antimonii* remains. A single exhaustion yields but little kermes; but by repeating the boiling several times, a large quantity of very fine kermes is obtained.

In some cases, a small quantity of sulphur is added to the fused mixture of sulphide of antimony and alkaline carbonate; *e. g.* according to Dollfuss, 100 pts. of sulphide of antimony, 4·7 parts of sulphur and 50 pts. of dry carbonate of soda; according to Trommsdorf, 100 : 6 : 50; according to the *Pharmac. Boruss. ed.* 5, 100 : 50 : 75; and according to Bucholz, 100 pts. of sulphide of antimony, 22 pts. of sulphur, and 150 pts. of carbonate of potash. These mixtures yield kermes in larger quantity and less contaminated with antimonic oxide, but of a dingy colour, probably because it contains more sulphantimoniate of sodium (or potassium). A mixture of 100 pts. of sulphide of antimony with 22 pts. of sulphur and 150 pts. of carbonate of potash, yields 63 pts. of dingy kermes, containing 29 per cent. of oxide. (Pagenstecher.) The fused mass dissolves in boiling water, with the exception of 11 pts. and yields 50 pts. of kermes containing 13·5 per cent. of oxide. With 100 pts. of sulphide of antimony, 25 pts. of sulphur, and 100 pts. of carbonate of potash, 45 pts. of kermes are obtained, contaminated with 9 per cent. of antimonic oxide. (Duflos.)

6. Grey sulphide of antimony is ignited with a mixture of charcoal and carbonate or sulphate of potash or soda, the resulting mass boiled with water, and the filtrate set aside to cool.—As the liquid cools, a gelatinous brown kermes separates, which consists of a compound of tersulphide of antimony with sulphide of potassium or sodium, and is totally different from officinal kermes. (Liebig.)

By fusing 100 pts. of sulphide of antimony with 100 pts. of black flux, exhausting the mass with water, and filtering hot, a solution is obtained, which solidifies on cooling to a brown jelly; this substance colours the water yellow, even after long-continued washing, and is very difficult to dry. But if carbonate of potash or soda is added to the hot filtrate before it gelatinizes, and the whole boiled for half an hour, officinal kermes is precipitated on cooling, in the form of a brilliant, finely divided powder, which is easily purified with water and dried. (Liebig.) —The mass obtained by strongly igniting a mixture of 100 pts. of sulphide of antimony and 200 pts. of black flux, yields, after exhaustion with water, a colourless filtrate, which yields nothing on cooling, but on the addition of alkaline carbonates, deposits a dense kermes free from oxide. (Liebig.) To this head likewise belongs the kermes prepared by exhausting with water the antimony-slag which covers the metal when reduced by cream of tartar and nitre. (p. 318, 2.)

When 100 pts. of sulphide of antimony are heated with 300 pts. of cream of tartar, till the latter is merely carbonized, a kermes containing oxide is produced, because the carbonate of potash formed exerts an oxidating action on the antimony. (Liebig.)—Again, if 100 pts. of sulphide of antimony are strongly ignited with 400 pts. of cream of tartar, 56 pts.

of metallic antimony are reduced, and the filtrate, after exhausting the mass with water, deposits nothing on cooling, and only a small quantity of brick-red kermes on the addition of acids. (Duflos.)

A mixture of 100 pts. of sulphide of antimony, 12·5 pts. of sulphur, 50 pts. of carbonate of potash, and 4 pts. of charcoal, yields metallic antimony; and the remainder dissolves almost entirely in boiling water, the solution depositing 48·4 pts. of kermes, free from antimonic oxide.—With 25 pts. of sulphur, 100 pts. of carbonate of potash, and 8 pts. of charcoal, 9 pts. of metallic antimony are obtained; and the residue dissolves in hot water and yields 16 pts. of kermes free from oxide. (Duflos.)

A mixture of 100 pts. of sulphide of antimony with 100 pts. of sulphate of potash and 17 pts. of charcoal, yields, after fusion and subsequent solution in hot water, from 83 to 100 parts of kermes. (Bucholz.) Pagenstecher obtained with these proportions, 22 pts. of kermes of a very bad colour, and containing 43 per cent. of oxide. Duflos likewise obtained but one-third as much as Bucholz, and the kermes contained 22·75 per cent. of oxide. This large quantity of oxide arises from the charcoal not being in sufficient quantity to convert the whole of the sulphate of potash into sulphide of potassium. Hence the sulphuric acid is but partly decomposed, and the potash set free converts a portion of the sulphide of antimony into antimonic oxide. (Duflos.)—A mixture of 100 pts. of sulphide of antimony, 100 pts. of sulphate of potash, and 25 pts. of charcoal, kept for some time at a red heat, yields 19 pts. of metallic antimony, and only 11 pts. of kermes free from antimonic oxide. Whence it appears that, in this case also, the sulphantimonite of potassium is, by prolonged fusion, partially resolved into sulphantimoniate of potassium and metallic antimony.—With 100 pts. of sulphide of antimony, 50 pts. of sulphate of potash, and 12·5 pts. of charcoal, 6 pts. of metallic antimony are obtained, together with a much larger quantity of kermes than in the former instance, and free from antimonic oxide. (Duflos.) The kermes prepared from sulphate of potash and charcoal forms a gelatinous mass, similar to that prepared with black flux. (Liebig.)

By boiling sulphide of antimony with an aqueous solution of protosulphide of sodium, and filtering, a solution is likewise obtained, which deposits a similar dingy kermes, containing a large quantity of sulphide of sodium. (Liebig.) A kermes having the same composition, is likewise precipitated, by dissolving sulphide of antimony in a boiling aqueous solution of protosulphide of potassium, and leaving the filtrate to cool. The kermes thus prepared, after washing with cold water, imparts sulphide of potassium with a small quantity of sulphide of antimony to boiling water, but cannot be entirely freed from sulphide of potassium even by long boiling. (Soubeiran, *J. Pharm.* 27, 294.)

7. An aqueous solution of sulphantimoniate of sodium is boiled with metallic antimony, till it is converted into a solution of sulphantimonite of sodium, and then precipitated by an acid.—Inasmuch as the sulphantimoniate of sodium may be freed from every trace of arsenic by crystallization, a kermes free from arsenic may be prepared from it, provided also that the metallic antimony used is free from that impurity. —A mixture of 100 parts of the crystallized compound, and 32 pts. of washed antimony, is boiled for an hour or two with 1000 pts. of water in a clean iron vessel, the water being replaced as it evaporates. The filtrate is then diluted with boiling water, and nearly saturated with dilute hydrochloric acid, whereupon 92 pts. of a fine reddish-brown

kermes, free from antimonic oxide, is deposited. (Duflos.)—If the sulphantimoniate of sodium is not freed from adhering soda by re-crystallization, or if the mixture is exposed to the air while cooling, or if unboiled water is used for diluting the filtrate or washing the product, the kermes may contain antimonic oxide. But if the quantity of hydrochloric acid added is less than sufficient to saturate the soda, so that the latter is only converted into bihydrosulphate of soda, the precipitation of the kermes is complete, and the hydrosulphuric acid converts any antimonic oxide that may be formed, into sulphide of antimony. (Duflos.)—Formerly Duflos filtered the boiling liquid, stirring frequently, into a solution of 16 pts. of common salt and 32 pts. of Glauber's salt in 640 pts. of water; these salts accelerated the separation of the kermes, which amounted to between 40 and 48 parts.

In the third, fourth, and fifth methods of preparing the kermes, it is usual to boil the solution decanted from the precipitated kermes, with the insoluble residue obtained on the previous boiling, as long as the filtrate continues to deposit good kermes on cooling.—In the third, fourth, fifth, and sixth methods, it is best to let the filtrate run into a large quantity of warm water, so that the kermes may be precipitated as the liquid cools. —The kermes is washed, first by subsidence and decantation, and afterwards on a filter with water freed from air by boiling, and still warm; because, according to Cluzel, water containing air gives rise to oxidation. Duflos recommends washing with boiling hot water, to remove the antimonic oxide. H. Rose recommends the same treatment, in order to remove the sulphantimoniate of potassium or sodium. The first portions of the hot wash-water deposit kermes on cooling, because the sulphide of potassium or sodium which is dissolved out, carries sulphide of antimony with it. By long treatment with boiling water, however, a portion of the kermes itself may be decomposed. (*Vid. infra.*) Hence the hot washing of Gay-Lussac and others cannot be employed. Liebig purifies the varieties of kermes obtained by the fourth, fifth, and sixth methods from the sulphide of potassium or sodium which they contain, by digesting them in dilute tartaric acid, washing with cold water, and, lastly, drying at ordinary temperatures.

Properties.—The kermes prepared by method 1 is a dense, fissured mass, having a specific gravity of 4·15 and a conchoidal fracture; it scratches grey antimony ore pretty strongly; has a dark leaden-grey colour, and when in thin plates, exhibits a dark hyacinth-red colour by transmitted light; it yields a reddish-brown powder, rather darker than that of ordinary kermes. (Fuchs.) Kermes obtained by process 2, is a brownish-red, loosely coherent powder. The kermes containing antimonic oxide, prepared by methods 3, 4, and 5, is a loosely agglomerated, reddish-brown powder, which, when rubbed on paper, leaves a brownish-red streak, (after washing with boiling water, a blackish-grey streak.) (Liebig.)—The kermes, rich in sulphantimoniate of potassium or sodium, obtained by method 6, dries up in hard brown masses, having a conchoidal fracture and yielding a brown powder.—When kermes, free from antimonic oxide, (method 1 or 2,) is slowly cooled after fusion, it is wholly converted into crystalline, radiated grey sulphide of antimony, which yields a blackish powder. Kermes, containing antimonic oxide, yields, on the contrary, a slag-like mass. (Fuchs.) Cold hydrochloric acid likewise converts kermes, in a few days, into grey sulphide of antimony. (Proust.)

Pure mineral kermes must be regarded, with Berzelius, H. Rose, and

Fuchs, as amorphous tersulphide of antimony. This view is confirmed by the following facts. Grey sulphide of antimony is converted by fusion and rapid cooling into the red sulphide. (Fuchs.) The kermes precipitated from salts of antimonic oxide by hydrosulphuric acid is free from antimonic oxide and water, and exhibits the colour and other properties of ordinary kermes. 153 pts. (1 At.) of antimonic oxide dissolved in a boiling solution of cream of tartar and precipitated by hydrosulphuric acid, yield a quantity of kermes amounting to 177·16 pts. after drying in a sand bath; this when fused loses 3·25 pts. of water, and leaves 173·91 pts. of grey sulphide of antimony. [The quantity of sulphide of antimony produced should be 177 pts. (1 At.); the slight difference is probably due to the presence of moisture in the antimonic oxide or to some incidental loss in the process.] When 100 pts. of the kermes thus obtained and dried in the sand-bath are dissolved in strong hydrochloric acid and precipitated by water, the resulting powder of algaroth amounts to 86·7 pts., while 100 pts. of grey sulphide of antimony treated in the same way yield 87 pts. Hence this kermes must consist of tersulphide of antimony with a small quantity of hydrosulphate of antimonic oxide [or water] adhering to it. (R. Phillips, *Ann. Phil.* 25, 378.) The kermes precipitated from 100 pts. of tartar-emetic by hydrosulphuric acid and dried in a water bath, fuses when heated in a glass tube drawn out to a fine point, yielding grey sulphide of antimony with loss of only 0·37 pts. ($\frac{1}{3}$ per cent.) of yellowish water containing a small quantity of hydrosulphuric acid and ammonia. [Robiquet, Gay-Lussac, and O. Henry likewise obtained ammoniacal water by heating kermes; probably the kermes absorbs ammonia from the air.] The conversion of kermes into grey sulphide of antimony takes place at a temperature considerably below redness, commencing at the part most heated, and extending throughout the whole mass; the portions adhering to the glass, however, partly retain their red colour. (Gmelin.) The kermes precipitated from tartar-emetic by hydrosulphuric acid and dried in a water bath, loses when fused only $\frac{1}{2}$ per cent. of hydrosulphuric acid, and is converted into grey sulphide of antimony. (Geiger & Reimann, *Mag. Pharm.* 17, 132.) According to Robiquet, the kermes obtained from tartar-emetic should yield 10 per cent. of water; but he does not state whether it must be previously dried, or in what manner.

The kermes obtained by methods 3, 4, and 5 contains variable and often large quantities of antimonic oxide (partly in combination with potash or soda) and smaller quantities of sulphantimoniate of potassium or sodium; that prepared by method 6 does not contain antimonic oxide, but a proportionably larger quantity of the latter compound, which gives it its dingy colour. The antimonic oxide in the kermes is not chemically combined with the sulphide of antimony, but merely mixed with it, in the form of crystals, so that it is best detected by the microscope. It contains little or no alkali. (H. Rose.) According to Liebig, however, the antimonic oxide is chemically combined, at least in part, with the sulphide of antimony. Liebig nevertheless remarks that the whole of the antimonic oxide and the compound of antimonic oxide and alkali may be removed by prolonged washing, leaving pure sulphide of antimony. When kermes containing antimonic oxide is fused in a stream of pure carbonic acid gas, the mass does not yield a pure grey powder, but a powder having a tinge of red or brown; very small quantities of antimonic oxide may however be better recognized under the microscope than by this method. (H. Rose.) A solution of cream of tartar boiled with pure grey sulphide of antimony or kermes free from oxide takes up but a mere trace of antimonic oxide—just sufficient to exhibit a red colour on treating the filtrate with hydrosulphuric acid gas. From freshly precipitated and still moist kermes containing antimonic oxide, the above solution separates a large quantity of the oxide, but after drying, not much more than from kermes originally free from antimonic oxide. (H. Rose.) But, according to Buchner and Pagenstecher, cream of tartar separates the antimonic oxide from kermes containing that substance, after drying and even after fusion. Kermes containing antimonic oxide likewise yields it to a hot solution of tartaric acid or to cold hydrochloric acid. Kermes containing antimonic oxide does not dissolve completely in the moist state in cold solution of potash, but leaves a yellow mixture of the compound of antimonic oxide and potash with sulphide of antimony. (Liebig.) If the kermes prepared by method 6, which contains no antimonic oxide, but sulphantimoniate of sodium, be dried at 65° (149° F.) it does not afterwards give off any water at 140° (284° F.); but when ignited in a current of hydrogen gas, it evolves the water of crystallization belonging to the sulphantimoniate: the sulphur-salt undergoes no further decomposition, but remains in the tube together with the reduced antimony. This kermes cannot be perfectly freed from the sulphur-salt, even by long-continued washing with hot water. (H. Rose.) In the moist state, it dissolves completely in cold solution of potash; and the solution, on the addition of acids, evolves hydrosulphuric acid and deposits sulphide of antimony. (Liebig.) When heated with tartaric acid, it gives off hydrosulphuric acid. (Liebig.)

The old theory, according to which kermes was regarded as hydrosulphate of antimonic oxide $= SbO^3,3HS$,—and the similar view of Buchner and Gay-Lussac, which regarded it as a hydrate of tersulphide of antimony, combined in part with antimonic oxide, are no longer tenable: for, if either of these views were correct, kermes should yield considerable quantities of water when heated.

Since the pure tersulphide of antimony obtained by methods 1 and 2 exhibits the red colour and the other characters of kermes, it follows that the presence, in variable proportions, of antimonic oxide, the compound of antimonic oxide and alkali, sulphantimoniate of potassium or sodium, and water, cannot be regarded as essential to the constitution of kermes. These substances, indeed, rather impair than heighten its colour. They all however—especially the antimonic oxide—increase the medicinal action of the kermes. But, as the amount of antimonic oxide is very variable, and may even differ when the same process is followed, according to the temperature at which the solution is cooled, and the time which elapses between the formation of the kermes and its separation from the liquid, &c., it is yet doubtful whether kermes free from antimonic oxide would not be preferable for medicinal purposes—inasmuch, as like the pentasulphide of antimony, it exerts a more powerful action than the grey sulphide, in consequence of its finer state of division and amorphous aggregation. And if in particular cases its power were required to be increased, definite quantities of antimonic oxide or tartar-emetic might be mixed with it. For this purpose, the kermes free from arsenic, prepared by methods 2, *a* and 7 would answer better than the kermes 2, *b*; but a kermes of this kind free from oxide may be most readily prepared by Liebig's process (p. 344).

[For analyses of kermes, chiefly of old date, and no longer satisfactory—especially as the hydrated sulphantimoniate of potassium or sodium was overlooked—*vid.* Cluzel, Thénard, Robiquet, Buchner, Brandes, and O. Henry, in the memoirs above quoted, p. 317.]

The following analyses are by H. Rose.—*a.* Kermes prepared by method 3, by boiling with carbonate of soda; not very carefully dried.—*b.* Kermes (3) prepared by boiling with carbonate of potash.—*c.* Kermes (4) obtained by boiling with solution of potash, slightly washed $=2SbS^3+KS,SbS^5+2Aq$.—*d.* The same, after long-continued washing with hot water $= 9SbS^3+KS,SbS^5$.

	a.	*b.*	*c.*	*d.*
Sb	67·81	69·00	61·91	67·08
S	28·24	28·41	30·26	29·44
Na	1·33	K 2·25	5·66	3·48
HO	2·62		2·17	
	100·00	99·66	100·00	100·00

Decompositions of Mineral Kermes.—Kermes undergoes the same decompositions as the grey sulphide of antimony; in the wet way, however, they are more readily produced, in consequence of the greater mechanical division of the kermes; the admixture of antimonic oxide may also occasion slight differences. It exhibits the following peculiar reactions:—1. When kermes free from antimonic oxide is brought in contact with a red-hot body in the open air, it becomes incandescent, and is converted into sulphurous acid, antimonious acid, and antimonic oxide (Liebig.)—2. When recently precipitated kermes is boiled for a long time with a large quantity of water, out of contact of air, it is completely resolved into hydrosulphuric acid gas and antimonic oxide, which remains dissolved in the water. If it be covered with a large quantity of water and exposed to the air, it disappears entirely after a while, with the exception of a few white flakes. (Geiger & Hesse, *Ann. Pharm.* 7, 19.) A. Vogel (*J. Pharm.* 8, 148) likewise found that water repeatedly boiled with kermes, extracted antimonic oxide from it at each boiling.—3. Kermes precipitated from tartar-emetic by hydrosulphuric acid forms with ammonia, a colourless solution, which again deposits kermes on exposure to the air. (Capitaine.) One part of kermes dissolves almost completely in 600 pts. of aqueous ammonia. (Garot.) Kermes containing antimonic oxide, *e. g.* that obtained by fusing 100 pts. of sulphide of antimony with 37·5 pts. of carbonate of potash, according to Berzelius' method (p. 345), is but very sparingly soluble in ammonia, either cold or hot, strong or dilute, so that acids produce but a scanty precipitate. The addition of milk of sulphur renders the kermes more soluble, because it induces the formation of pentasulphide of antimony, which is accordingly precipitated from the solution by acids. Hence ammonia serves to detect the presence of pentasulphide of antimony in kermes. (Geiger.)—4. Freshly precipitated and still moist kermes evolves heat when mixed with hydrate of potash, and forms a lemon-yellow mass, from which water extracts sulphide of potassium, sulphide of antimony, and a small quantity of the compound of antimonic oxide and potash, leaving a yellow mixture (crocus containing potash) of the latter compound with a compound of kermes and antimonic oxide. (Berzelius.) From the filtrate, bicarbonate of potash throws down a dense brown precipitate, consisting of a compound of 3 atoms of tersulphide of antimony with 1 atom of sulphide of potassium mixed with antimonic oxide, from which the combined potash has been separated by the carbonic acid. The supernatant liquid evolves hydrosulphuric acid on the addition of acids, and deposits a small quantity of pentasulphide of antimony, formed by the action of the air. With monocarbonate of potash, the solution solidifies, after a while, forming a brown jelly, in consequence of the separation of the same compound. This compound is also frequently precipitated in the gelatinous form, on diluting the liquid with water, because the power of the sulphide of potassium to dissolve the sulphide of antimony is diminished by dilution. (Liebig.) The kermes precipitated from hydrochlorate of antimonic oxide by hydrosulphuric acid, is rapidly and completely dissolved by an excess of cold dilute solution of potash, because the quantity of potash is sufficient to combine with the antimonic oxide, and that of the water is sufficient to dissolve the resulting compound. The colourless solution deposits the whole of the antimony in the form of sulphide of antimony, on the addition of hydrochloric acid, without evolving any hydrosulphuric acid gas. Carbonate of ammonia added to the dilute solution likewise precipitates all the antimony and sulphur, in the form of yellowish-red kermes; bicarbonate of potash or soda acts in a similar manner, but the brownish-red gelatinous precipitate which it throws down, consists of 3 atoms of tersulphide of antimony, 1 atom of sulphide of potassium, and more or less antimonic oxide; monocarbonate of potash or soda causes the liquid to gelatinize after a while; the precipitate has the same composition. When antimonic oxide or powder of algaroth is digested with a solution of kermes in caustic potash, it separates the whole of the sulphide of antimony, and forms a brown compound of sulphide of antimony, antimonic oxide, and potash. The solution rapidly absorbs oxygen from the air and deposits brilliant crystals of antimonite of potash, after which it contains sulphantimoniate of potassium. By boiling tersulphide of antimony prepared in the moist way with solution of potash, a solution is formed containing the same elements, but a larger proportion of sulphide of antimony, which is deposited on cooling, in combination with a small quantity of sulphide of potassium and antimonic oxide. The filtered solution yields with bicarbonate of potash, a precipitate consisting of sulphide of antimony with a small quantity of sulphide of potassium, but free from antimonic oxide. The solution obtained by treating grey sulphide of antimony with solution of potash and filtering from the residual crocus, behaves precisely in the same manner. (Liebig.) Kermes, while still moist, likewise dissolves readily in solution of soda, but much more slowly after drying, and forms a solution which is colourless and transparent at first, but becomes turbid on exposure to the air, and deposits a greyish-white powder of antimonious acid. (Geiger.) Kermes is easily soluble in hydrosulphate of ammonia. (Buchner.) It does not dissolve in the aqueous solution of sulphurous acid. (Berthier.) [For its decomposition with calomel, vid. *Mercury*, vol. VI.]

Compounds of Tersulphide of Antimony.—*a.* With Antimonic oxide. —*b.* With Basic Metallic Sulphides, forming salts called SULPHANTIMONITES. In these compounds, the tersulphide of antimony plays the part of a very feeble acid. Of the native compounds of this class, the most abundant are those of tersulphide of antimony with the sulphides of lead, iron, copper, and silver; they contain 1, $1\frac{1}{3}$, $1\frac{1}{2}$, 2, 3, 4, 6, or 9 atoms of the basic metallic sulphide, united with 1 atom of tersulphide of antimony.—In these sulphur-salts, tersulphide of arsenic and tersulphide of antimony replace each other, without any change in the crystalline form of the compound. (H. Rose, *Pogg.* 15, 414, and 587; 28, 435.)—

The compounds obtained by fusion with sulphide of potassium or sodium, constitute the ordinary *Liver of antimony, Hepar antimonii*, which, when it contains but little sulphide of antimony, is perfectly soluble in hot water, but when it contains a larger quantity, dissolves, with partial separation of the latter substance. On cooling, the solution deposits a portion of the tersulphide, in the form of kermes, and the remainder is precipitated by acids, even by carbonic acid.

B. *Tetrasulphide of Antimony?*—Formed when hydrosulphuric acid gas is passed through a solution of antimonious acid or antimoniate of potash in hydrochloric acid. (Berzelius, H. Rose.)—Yellowish-red powder, resembling sulphide of gold.—When heated, it evolves 1 atom of sulphur, and is converted into grey sulphide of antimony. It dissolves in boiling hydrochloric acid, and forms hydrochlorate of antimonic oxide, hydrosulphuric acid gas being evolved and sulphur deposited. (Berzelius.) Dissolves in ammonia, forming a yellow solution. (Capitaine.) Probably a mere mixture of tersulphide and pentasulphide of antimony.

	Calculation.		H. Rose.	
Sb	129	66·84	66·14	66·55
4S	64	33·16	33·86	33·45
SbS^4	193	100·00	100·00	100·00

C. PENTASULPHIDE OF ANTIMONY, ANTIMONIC SULPHIDE, SULPHANTIMONIC ACID.—*Golden Sulphuret of Antimony, Spiessglanzschwefel. Goldschwefel, Sulphur Antimonii auratum.*—Known only in the amorphous state.—*Formation* and *Preparation.*—1. By passing hydrosulphuric acid gas through a mixture of pentachloride of antimony with water and tartaric acid, and then collecting the precipitate (H. Rose); or by passing hydrosulphuric acid gas through antimonic acid diffused in water. (Berzelius.)—2. An aqueous solution of the sulphide of an alkali-metal, (*e. g.*, potassium, sodium, barium, calcium,) with sulphide of antimony and sulphur, is prepared as in the formation of kermes, the quantity of the sulphur being such, that the solution shall contain pentasulphide of antimony together with the protosulphide of the alkali-metal. For this purpose, sulphur is added to the mixture of tersulphide of antimony and the alkaline ingredients, either during the fusion or the subsequent boiling with water, in quantity sufficient to convert the tersulphide of antimony into pentasulphide. Or the change may be effected by exposing an aqueous solution of the alkaline sulphantimonite to the air, because the oxygen of the air combines with a portion of the alkali-metal, and the sulphur thereby liberated unites with the tersulphide of antimony.—From the solution of sulphantimoniate of potassium, sodium, &c. thus obtained, the pentasulphide of antimony is precipitated by the addition of a stronger acid, while the sulphide of the alkali-metal gives off hydrosulphuric acid, and is converted into an alkaline salt. For example:

$$3NaS,SbS^5 + 3SO^3 + 3HO = 3(NaO,SO^3) + 3HS + SbS^5.$$

If an excess of sulphur be added to the boiling solution, pentasulphide of the alkali-metal may be formed, in addition to the sulphantimoniate; and in that case, the addition of an acid precipitates pentasulphide of antimony from the latter compound, and milk of sulphur from the former, whereby a paler golden sulphide is produced.

a. Methods involving the use of solvents only.—A caustic alkali is boiled with grey sulphide of antimony, sulphur, and water, and the filtrate precipitated by an acid, which forms a soluble salt with the alkali.—During the ebullition, antimoniate of the alkali and sulphantimoniate of the alkaline-sulphide are produced, and, according to Mitscherlich, in the following manner, taking soda for example:

$$18NaO + 8SbS^3 + 16S = 3(NaO,SbO^5) + 5(3NaS,SbS^5).$$

The antimoniate of soda formed, remains for the most part undissolved If we assume that the filtrate contains only $3NaS,SbS^5$, then with 3 atoms or more of SO^3 and the decomposition of 3 atoms of water, we obtain the following products:

$$3NaO,SbS^5 + 3SO^3 + 3HO = (3NaO,SO^3) + SbS^5 + 3HS.$$

But inasmuch as a small quantity of antimoniate of soda is also dissolved from which the sulphuric acid sets the antimonic acid free, the latter is also converted, by the decomposition of a portion of the disengaged hydrosulphuric acid, into SbS^5.

α. A mixture of 1 pt. of grey sulphide of antimony and 1 pt. of sulphur is boiled with solution of potash or soda, and the liquid diluted filtered, and precipitated by dilute sulphuric acid. (Westrumb.)

β. A mixture of 1 pt. of sulphide of antimony and 1½ of sulphur is similarly treated (Göttling); the precipitate in this case is too pale.

γ. A mixture of 72 pts. (8 At.) of grey sulphide of antimony, 13 pts. (16 At.) of sulphur, 48 pts. (18 At.) of dry carbonate of soda, and 52 pts. (36 At.) of lime, is boiled and treated as above (18 atoms of lime would be sufficient to separate the carbonic acid from the carbonate of soda; the excess of lime is used merely to accelerate the decomposition). (Mitscherlich, *J. pr. Chem.* 19, 458.)

δ. The method of displacement may also be employed, exactly as in the preparation of kermes, (p. 344,) excepting that to the mixture of 2 pts. of finely powdered sulphide of antimony, 4 pts. of dry carbonate of potash or soda, 6 pts. of slaked lime, and 8 pts. of washed sand, an additional 1 pt. of flowers of sulphur must be added. The filtrate, on being precipitated with hydrochloric acid, yields a very brilliant golden-coloured sulphide, the quantity of which is nearly equal to that of the sulphide of antimony originally used. (Musculus, *J. Pharm.* 22, 241.)

ε. A mixture of 1 pt. of sulphide of antimony with 1 pt. of sulphur, 2 pts. of lime, and 8 pts. of water, is boiled for an hour, the water being replaced as it evaporates, and the filtrate precipitated by hydrochloric acid. The insoluble residue is again twice exhausted with water. (Abesser, *Repert.* 9, 274.)

ζ. Boiling solution of potash is saturated with sulphur; and for every 7 pts. of sulphur dissolved, 13 pts. of powdered metallic antimony are added, and the whole boiled for a quarter of an hour; the solution is then diluted, filtered, and precipitated by sulphuric acid. A portion of sulphur is however mixed with the pentasulphide, in consequence of the decomposition of hyposulphite of potash. (Duflos.)

η. 55 pts. of protosulphide of potassium, obtained by igniting sulphate of potash with ⅕ its weight of charcoal, is dissolved in 165 pts. of water, and the mixture boiled with 40 pts. of sulphur till it disappears. The solution is then filtered from charcoal; boiled with 64 pts. of finely powdered antimony, till the metal is completely dissolved; again filtered, diluted, and precipitated by sulphuric acid. (Duflos, *Br. Arch.* 29, 94; 31, 94.)

b. Methods, in which the sulphide of antimony is first ignited with a substance containing alkali.

aa. With an alkaline sulphate and charcoal. The charcoal converts the sulphate into a metallic sulphide; and by subsequent boiling with water and sulphur, the tersulphide of antimony is converted into pentasulphide.

α. A mixture of 6 pts. of grey sulphide of antimony with 16 pts. of monosulphate of potash, and 3 pts. of charcoal is fused, and the resulting mass boiled with 1 pt. of sulphur and 6 times its weight of water,—then diluted, filtered, and precipitated with sulphuric acid. (Bucholz, Trommsdorff.)

β. A mixture of 12 pts. of sulphide of antimony, 24 pts. of bisulphate of potash, and 4½ pts. of charcoal is fused at a gentle heat, with frequent stirring, till a portion dissolved in water, supersaturated with hydrochloric acid, and filtered, gives but a slight cloud with chloride of barium; the mass is then boiled with water and 3 pts. of sulphur for a few minutes, till the black colour of the liquid changes to pure pale yellow (by longer boiling, sulphide of antimony would be precipitated); after which, the solution is filtered and precipitated by an acid. The product is 15 pts. of pentasulphide of antimony. (Geiger, *Repert.* 9, 251.)

γ. Schlippe's crystallized sulphantimoniate of sodium, prepared by either of the methods given on page 385, is dissolved in water, and precipitated by sulphuric acid. (Schlippe, *Schw.* 33, 323.) The crystals must be treated with cold water, (so that the kermes may be left undissolved,) and the solution afterwards filtered: hot water dissolves the kermes also, and the resulting solution yields a darker preparation on the addition of acids. (Jahn, *N. Br. Arch.* 22, 43.) By washing the crystals of Schlippe's salt several times with cold water, reducing them to fine powder, digesting them with 14 times their weight of cold water for 24 hours, with frequent stirring—filtering from kermes—and precipitating as above—a sulphide is obtained, always having the same intensity of golden colour. (Artus, *J. pr. Chem.* 27, 381.)

δ. A mixture of 4 pts. of sulphide of antimony with 16 pts. of heavy spar and 4 pts. of charcoal is ignited—the resulting mass boiled with water and 1 pt. of sulphur—and the liquid filtered and precipitated by hydrochloric acid. In this process chloride of barium is likewise obtained. (Lampadius, Trommsdorff, *N. Tr.* 1, 1, 33.) Strong and continued ignition is necessary to ensure the success of the process: moreover, unless the product is carefully washed, the pentasulphide of antimony may contain a portion of the poisonous chloride of barium.

bb. Sulphide of antimony is fused with sulphur and an alkaline carbonate, the product dissolved in water, and the filtrate precipitated by an acid. In this case, either a decomposition into alkaline antimoniate and sulphantimoniate of the alkali-metal takes place—similar to that described by Mitscherlich, in the preparation by the method of solution, (p. 355,)—or, as in the formation of kermes: 3KO and SbS^3 are resolved into 3KS and SbO^3, whereupon the 3KS take up the remaining SbS^3, which is converted into SbS^5 by the sulphur.

The following proportions of grey sulphide of antimony, sulphur, and carbonate of potash are recommended; 30 : 6 : 24. (Berzelius.)—

30 : 15 : 90. (Wieglieb.)—30 : 30 : 50. (Westrumb.)—30 : 60 : 120. (Hirsching.)

Properties.—Yellowish-red powder or loosely agglomerated mass, having a very feeble smell of sulphur and a sweetish sulphurous taste; slightly emetic.

	Calculation.		
Sb	129	....	61·72
5S	80	....	38·28
SbS^5	209	....	100·00

The pentasulphide of antimony prepared by method 1, after being dried at a gentle heat, contains neither hydrogen nor oxygen, but consists of 1 atom of antimony combined with 5 atoms of sulphur; and accordingly, when ignited in a current of hydrogen gas, it yields metallic antimony, sublimed sulphur, and hydrosulphuric acid gas, but no water. (H. Rose, Berzelius.) But according to Thénard, Geiger, and Buchner, who have also given analyses of the pentasulphide, it either contains water already formed, or the elements of water, which are evolved in the form of water on heating the compound.

Decompositions.—1. When heated out of contact of air—according to Mitscherlich, even at the boiling point of sulphur—it gives off 2 atoms of sulphur and is converted into grey sulphide of antimony.—2. Swells up in the fire and burns with flame (whereas kermes does not exhibit any appearance of flame). (A. Vogel.)—3. When it is exposed to the air in the moist state for a few days, or in the dry state in as many months, a very small portion of it is decomposed, yielding a small quantity of antimonic oxide, which may be separated by a boiling solution of cream of tartar. The emetic properties of pentasulphide of antimony may perhaps be referred to this decomposition. (Otto, *Ann. Pharm.* 26, 88; Jahn, *N. Br. Arch.* 22, 43.)—4. Chlorine water and nitric acid render it paler, probably by oxidation. (Pagenstecher, *N. Tr.* 3, 1, 391.)—5. Cold strong hydrochloric acid turns it grey (Geiger) [probably by resolving it into grey sulphide of antimony and free sulphur]; but hot hydrochloric acid dissolves it, producing hydrated terchloride of antimony, disengaging hydrosulphuric acid, and separating sulphur.—6. Pure pentasulphide of antimony dissolves in about 50 parts of cold dilute solution of ammonia, leaving only a slight residue; on the application of a gentle heat, it dissolves completely. When it contains too small a proportion of sulphur, kermes remains undissolved; if it contains an excess, sulphur is left behind. Occasionally also a small quantity of antimonious acid is found in the residue. The yellow ammoniacal solution when treated with acids, again deposits the pentasulphide without evolution of hydrosulphuric acid. (Geiger, *Mag. Pharm.* 29, 241.) On dissolving the pentasulphide in ammonia, $3NH^4S,SbS^5$ is formed, and antimonic acid left behind (possibly mixed with a small quantity of sulphur). (Rammelsberg.) The solution when boiled deposits tersulphide of antimony and free sulphur. (Capitaine.)—7. Golden sulphide of antimony dissolves rapidly in cold solution of soda, forming a yellow liquid. (Geiger.) On boiling this solution, antimoniate of soda is separated and a solution of sulphantimoniate of sodium formed. (Mitscherlich.) It dissolves in moderately strong solution of potash with separation of antimoniate of potash, and from the solution diluted with water, bicarbonate of potash precipitates brown sulphantimoniate of potassium containing an excess of the sulphur-acid (*see* *this compound*); the filtrate, on being treated with acids, still evolves hydrosulphuric acid and deposits a small quantity of pentasulphide of antimony. (Rammelsberg.) The solution in caustic potash is at first transparent; but if left overnight, deposits a crystalline precipitate (Jahn) [of antimoniate of potash.] A cold solution of carbonate of potash does not sensibly affect pentasulphide of antimony; but on boiling, it evolves carbonic acid gas and behaves like caustic potash, viz. precipitating antimoniate of potash and forming a solution of sulphantimoniate of potassium. Baryta-water behaves like solution of potash, but separates a larger quantity of antimoniate; the solution contains $3BaS,SbS^5$. (Rammelsberg, *Pogg.* 52, 204)—8. When immersed in an aqueous solution of nitrate of silver, it turns brown, and on boiling becomes black, forming a mixture of sulphantimoniate of silver and antimonic acid. A similar effect is produced with a solution of sulphate of copper. (Rammelsberg.) —9. Decomposed by calomel (*vid. Calomel*).—10. Gives up sulphur to boiling bisulphide of carbon and to boiling oil of turpentine. According to Mitscherlich, the bisulphide of carbon separates 2 atoms of sulphur and leaves tersulphide of antimony; according to Rammelsberg, it extracts only 2 per cent. after a quarter of an hour's boiling.—11. When mixed with saccharine solutions which are undergoing the vinous fermentation, it disengages hydrosulphuric acid. (Pagenstecher.)

Compounds.—With Basic Metallic Sulphides, forming salts called SULPHANTIMONIATES. These are obtained: 1. By fusing together pentasulphide of antimony or a mixture of tersulphide of antimony and sulphur, with the sulphide of an alkali-metal, or with charcoal and a fixed alkaline carbonate or sulphate. If a strong heat be used, the addition of sulphur to the tersulphide of antimony is not necessary, because, at a high temperature, it is resolved into pentasulphide and metallic antimony. —2. By dissolving pentasulphide of antimony in aqueous solutions of the alkaline hydrosulphates; if the bihydrosulphates are used, half the hydrosulphuric acid is expelled.—3. By dissolving pentasulphide of antimony in the solution of a caustic alkali, or of an alkaline carbonate at a boiling heat. In this process, antimoniate of the alkali is formed at the same time, and is deposited almost completely in the form of a white powder. —4. By decomposing aqueous solutions of the terbasic alkaline antimoniates by a current of hydrosulphuric acid gas.

$$3KO,SbO^5 + 8HS = 3KS,SbS^5 + 8HO.$$

If the alkaline mono-antimoniates are used, $\frac{2}{3}$ of the antimonic acid is precipitated in the form of pentasulphide of antimony.—5. The compounds containing the heavy metals are obtained by gradually adding a solution of one of their salts to a solution of the sulphantimoniate of an alkali-metal—the latter being in excess. When the heavy metallic salt predominates, the precipitated sulphantimoniate and the remaining metallic salt decompose each other, especially on boiling; and the precipitate formed in this manner, with lead, copper, or silver, contains 1 atom of antimony, 8 atoms of the other metal, 8 atoms of sulphur, and 5 atoms of oxygen, and is probably a mixture of 8 atoms of metallic sulphide and 1 atom of antimonic acid: *e. g.* In the case of lead: $3PbS,SbS^5$ is first precipitated; and this, with $5PbO$ contained in the solution, forms $8PbS + SbO^5$. Generally speaking, these compounds contain 3 atoms of the basic metallic sulphide with 1 atom of pentasulphide of antimony. Those of the alkali-metals are colourless or yellow; sustain a red heat without decomposition, when heated out of contact of air; and are soluble in water, but not in alcohol. Their aqueous solutions are slowly decomposed in the air, yielding carbonate and hyposulphite of the alkaline base and depositing kermes; all acids, including even the carbonic, decompose them, liberating hydrosulphuric acid and precipitating pentasulphide of antimony. According to Liebig, they are not precipitated by carbonate of ammonia, nor, according to H. Rose, by monocarbonate of potash or soda, a property which serves to distinguish them from solutions of the tersulphide of antimony in sulphides of the alkali-metals. The compounds of pentasulphide of antimony with heavy metallic sulphides are yellow, reddish-yellow, brown, or black; give off two atoms of sulphur and leave $3MS\,SbS^3$ when ignited out of contact of air; and are for the most part insoluble in water. (Rammelsberg.)

D. OXY-SULPHIDE OF ANTIMONY.—*a. Regulus Antimonii medicinalis.*—*Rubinus Antimonii.*—This compound is prepared by fusing a mixture of 5 parts of grey sulphide of antimony and 1 part of carbonate of potash, and separating the upper stratum (consisting of sulphantimonite of potassium) from the lower. Black mass, having a brilliant conchoidal fracture, and yielding a dark red powder. It appears to be a compound of tersulphide of antimony with a very small proportion of antimonic oxide.

b. Red Antimony-ore. — *Antimony-blende.* — (*Rothspiessglanzerz.*) — Occurs in needles, having the form of oblique rhombic prisms; *i* : *m* = 101° 19′. According to Bernhardi (*Br. Arch.* 21, 4), it has the same crystalline form as grey antimony-ore, and is moreover formed by its decomposition. (*vid.* Blum, *Pseudomorphosen*, 172.) Specific gravity = 4·6; softer than gypsum; cherry-red, slightly translucent, appearing scarlet by transmitted light; has a diamond lustre; fuses very readily before the blowpipe, sinking into the pores of the charcoal, and volatilizing in dense clouds. When treated with hot concentrated hydrochloric acid, it gives off hydrosulphuric acid. According to H. Rose (*Pogg.* 3, 452), when ignited in a current of hydrogen gas, it yields hydrosulphuric acid, water, and antimony. The same compound, containing 17·94 per cent. of sulphur, but of an orange colour, is sublimed when aqueous vapour is passed over ignited sulphide of antimony. (Regnault.)

	Red Antimony-ore.		H. Rose.		
3Sb	387	76·33	75·66	to	74·45
6S	96	18·93	20·49	,,	20·49
3O	24	4·74	4·27	,,	5·29
$SbO^3,2SbS^3$	507	100·00	100·42	,,	100·23

Or:

SbO^3	153	69·82
$2SbS^3$	354	30·18
	507	100·00

c. Antimonial Saffron. — *Metallic Saffron.* — *Spiessglanz-safran.* — *Crocus Antimonii s. Metallorum.*

a. Free from Potash.—1. Prepared by fusing a mixture of 3 parts of antimonic oxide and 1 part of tersulphide of antimony, or a mixture of antimonic oxide, antimonious acid, or antimonic acid, with the proper proportion of sulphur. (Proust.)—2. By diffusing freshly precipitated kermes in acid hydrochlorate of antimonic oxide, and adding water till antimonic oxide begins to separate; the antimonic oxide is taken up by the kermes. (Berzelius.) Brownish-yellow. Converted into kermes by aqueous hydrosulphuric acid or hydrosulphate of ammonia.

β. Containing Potash.—When the mass obtained by igniting a mixture of 1 part of grey sulphide of antimony with $\frac{1}{2}$....1 part of carbonate of potash or 1 part of nitre, is exhausted with hot water, a yellowish-brown mixture remains consisting of oxysulphide of antimony and the compound of antimonic oxide and potash. According to Liebig, the quantity of potash amounts to between 12 and 16 per cent. A similar but yellower crocus is obtained by treating the grey sulphide of antimony with boiling solution of potash, or the red sulphide of antimony with the same solution cold. Crocus fuses when heated, forming a transparent yellowish glass. Dilute hydrochloric acid extracts the compound of antimonic oxide and potash, and likewise separates part of the antimonic oxide from the oxysulphide. (Berzelius.)

d. Glass of Antimony.—*Spiessglanzglass, Vitrum Antimonii.*—This compound is prepared by roasting sulphide of antimony on the iron hearth of a reverberatory furnace, stirring constantly by means of a rake, and regulating the temperature so that the sulphide may neither melt nor burst into flame, but only give off a moderate quantity of fumes. The heat is then gradually raised to low redness, till sulphurous acid ceases to pass off, and the sulphide of antimony is converted into antimonious acid. The antimony-ash, as it is called, is next rapidly fused in a covered earthen crucible with about $\frac{1}{20}$ of its weight of grey sulphide of antimony, till its molten surface becomes bright like a mirror; it is then poured out on a marble slab or a polished plate of copper. A mixture of 100 pts. of the antimony-ash with 3·35 pts. of sulphide of antimony, yields a reddish-yellow, transparent glass; with 4·39 pts., a yellowish-red transparent glass; with 5·28 pts., a hyacinth-red transparent glass; and with 6·69 pts., a dark hyacinth-red translucent glass. (Werner, *J. pr. Chem.* 12, 53.) The antimonious acid is reduced by a portion of the sulphide of antimony to antimonic oxide, with evolution of sulphurous acid, and in this form combines with the remaining sulphide of antimony. Or again, the roasting may be stopped before the whole of the sulphide of antimony is decomposed, in which case no addition of sulphide is required previous to fusion; but then it is more difficult to ensure the proper proportions. The mixture should be stirred with a pipe-stem, because when iron is used, it is apt to contaminate the glass. According to Proust, this compound may be prepared by fusing together 8 parts of antimonic oxide and 1 part of sulphide of antimony, or by fusing either of the three higher oxides of antimony with a quantity of sulphur smaller than that which is required to form crocus of antimony.

Brilliant; appears reddish-black by reflected, and dark hyacinth-red by transmitted light.—Contains, according to Proust, 88·9 per cent. of antimonic oxide and 11·1 of sulphide of antimony; according to Soubeiran (*J. Pharm.* 10, 528) 91·5 per cent. of antimonic oxide, 1·9 of sulphide of antimony, 4·5 of silica, and 3·2 of ferric oxide.—When treated with acids, it gives up antimonic oxide; with hot hydrochloric acid it evolves hydrosulphuric acid gas.—Glass of antimony may be fused with silica (*e.g.* from the crucible) and with glass, the products being hyacinth-coloured glasses.

E. Sulphite of Antimonic Oxide.—Formed when antimonic oxide is digested with aqueous solution of sulphurous acid, or when sulphurous acid gas is passed through acid hydrochlorate of antimonic oxide. Insoluble in water. (Berzelius.)

F. SULPHATE OF ANTIMONIC OXIDE.—When antimony is heated with oil of vitriol; the products are sulphurous acid, sublimed sulphur, and a white anhydrous residue, which is probably the salt *c*.

a. Disulphate ?—1. Formed by digesting the above-mentioned white residue in cold water, whereby sulphuric acid and a small quantity of antimonic oxide are separated.—2. By dissolving 1 part of the white residue in 2 parts of water, enough oil of vitriol being added to render the liquid clear, and then precipitating by water. (Brandes.) White powder containing 3 per cent. of water. When boiled with water, it loses the greater part of the sulphuric acid, so that 99 parts of antimonic oxide retain no more than 1 part of sulphuric acid. (Brandes.) ¶ Peligot has since examined this compound and shown that it is really a disulphate. (*Ann. Chim. Phys.* 3, 20, 283.) ¶

b. Monosulphate.—Formed by reducing the salt *c* to powder, agitating with alcohol, collecting the resulting powder on a filter, and drying it. (Brandes.)

¶ *c. Bisulphate.*—Obtained by treating powder of algaroth with fuming sulphuric acid; crystallizes in small brilliant crystals. (Peligot.) ¶

d. Tersulphate.—1. The white residue obtained by heating antimony with oil of vitriol?—2. Crystallizes in small needles from a solution of the white compound in excess of sulphuric acid. (Brandes.)—The white residue, when ignited, evolves sulphurous acid and oxygen gas (Gay-Lussac), together with anhydrous sulphuric acid (Bussy), and often yields a sublimate of antimonic oxide in the form of needles. (Bucholz.) When ignited in a current of hydrogen gas, it yields a mixture of antimony, sulphide of antimony, and antimonic oxide. (Arfvedson, *Pogg.* 1, 24.) The salt is converted by water, either into *a* or into nearly pure antimonic oxide, according to the temperature of the water.

¶ *e. Quadrosulphate.*—When powder of algaroth is treated with concentrated sulphuric acid (SO^3, HO) hydrochloric acid gas is evolved, and quadrosulphate of antimony obtained in needles, which can only be dried by keeping them for a long time on a piece of burnt clay in vacuo over oil of vitriol. (Peligot.) ¶

By digesting *c* in strong sulphuric acid, a sulphate is formed containing excess of acid.

	At.	*a, Ignited.*		Brandes.	Peligot.
SbO^3	2	306	88·44	90·72	88·6
SO^3	1	40	11·56	9·28	11·4
	1	346	100·00	100·00	100·0

	At.	*b.*		Brandes.
SbO^3	1	153	79·3	78·10
SO^3	1	40	20·7	21·25
	1	193	100·0	99·35

				Peligot.	
	At.	*c.*		(1)	(2)
SbO^3	1	153	65·6	63·0	64·3
SO^3	2	80	34·4	37·1	35·0
	1	233	100·0	100·1	99·3

	At.		d.	Brandes.
SbO^3	1	153	56·04	56·4
SO^3	3	120	43·96	43·2
	1	273	100·00	99·6

				Peligot.	
	At.		e.	(1)	(2)
SbO^3	1	153	48·8	50·2	44·3
SO^3	4	160	51·2	51·9	53·1
	1	313	100·0	102·1	97·4

Antimonious acid is sparingly soluble in oil of vitriol. (Berzelius.)

ANTIMONY AND SELENIUM.

A. SELENIDE OF ANTIMONY.—The two elements readily unite on the application of heat, the temperature during combination frequently rising to redness. The product is a lead-grey mass, which fuses at a red heat—has a crystalline fracture—and when heated in the air, gives off a small quantity of selenium and becomes covered with a vitreous slag. A similar compound is precipitated from a solution of tartar-emetic by hydroselenic acid gas. (Berzelius.)

B. OXY-SELENIDE OF ANTIMONY.—The two compounds fuse readily together, yielding a brownish-yellow, translucent, vitreous mass, like glass of antimony. (Berzelius.)

ANTIMONY AND IODINE.

A. TERIODIDE OF ANTIMONY.—The two elements unite at ordinary temperatures, the combination being attended with great rise of temperature and evolution of iodine vapour, and even with explosion, if large quantities are used.—On one occasion, when a few ounces of the mixture were put into a retort, the retort burst with a loud report, even before heat was applied, and the compound was thrown up to the ceiling of the laboratory. (Brandes, *N. Br. Arch.* 21, 319.)—When powdered antimony is added to iodine, the first portions render the iodine fluid; after which the antimony must be gradually added till saturation is effected. (Serullas, *J. Pharm.* 14, 19.) Or a mixture of 129 parts (1 At.) of antimony, and not quite 378 parts (3 At.) of iodine is heated in a retort, and the resulting compound separated from the excess of antimony by distillation. (Brandes, *N. Br. Arch.* 14, 135; 17, 283.)—Crystalline, brownish-red mass, which yields a cinnabar-red powder. (Serullas.) Has a semi-metallic lustre; becomes blackish-red every time it is heated; and at higher temperatures softens, and afterwards fuses to a dark garnet-red liquid, which evolves violet-red vapours at first, but afterwards, when more strongly heated, gives off scarlet vapours, and either sublimes in the form of a scarlet film, or distils over in the liquid state. (Brandes.) The distillation takes place at a moderate heat (Serullas), a little above the boiling point. (Berthemot.)

	Calculation.		Brandes.
Sb	129	25·44	25·5
3I	378	74·56	
SbI^3	507	100·00	

Nitric acid is coloured yellow by iodide of antimony; if heat be applied, violent action takes place, and iodine is set free.—When iodide of antimony is treated with oil of vitriol at ordinary temperatures, the iodine is separated with great rapidity.—Hydrochloric acid dissolves iodide of antimony, forming a yellow liquid which is precipitated white by water.—When it is mixed with cold solution of ammonia, hydriodate of ammonia is formed, with separation, first of a yellow, and afterwards of a yellowish-white powder. (Brandes.)—Water resolves iodide of antimony into yellow pulverulent oxy-iodide of antimony and a reddish yellow liquid, which may be regarded as solution of iodide of antimony in aqueous hydriodic acid, or as an aqueous solution of acid hydriodate of antimonic oxide.—In this case, two-thirds of the iodine are separated by the water. (Serullas.) Spirit containing 80 per cent. of alcohol behaves like water; the yellow powder separated by it amounts to one-fourth of the iodide of antimony used; the reddish-yellow liquid, when distilled, yields free iodine and a second reddish-yellow liquid, having the odour of horse-radish, and leaves a brownish-red substance containing 33·4 per cent. of antimony. (Brandes.)

B. HYDRATED OXY-IODIDE OF ANTIMONY or BASIC HYDRIODATE OF ANTIMONIC OXIDE.—The pale yellow powder, separated by decomposing teriodide of antimony with water, has this composition.—Even when dried at a temperature at which it begins to decompose, it still gives off water if more strongly heated, and likewise yields a sublimate of iodide of antimony and a residue of antimonic oxide. It may be deprived of the whole of its iodine by repeated washing with small quantities of water. (Serullas.)—If it be washed with boiling water till the filtrate no longer reddens litmus, and the washing still further continued, it is partially decomposed, and the water deposits micaceous scales on cooling. When this compound is boiled in water with zinc or iron (tin acts less readily), antimony is reduced in the form of a black powder. Alkalis and magnesia, or their carbonates, separate antimonic oxide and dissolve an iodide of the alkali metal. (Berthemot.)—Brandes & W. Böttger regard the compound as SbI^2, because in their analysis they obtained 61·77 parts of antimony to 34·76 parts of iodine,—and on heating the compound in a narrow glass tube, teriodide of antimony was sublimed, and metallic antimony left, together with a mere trace of antimonic oxide [the author obtained as residue, a yellow glass consisting of antimonic oxide with a small quantity of iodide of antimony]; nevertheless they add, that when digested with potash, the compound left a perfectly white powder, and that it dissolved completely in a warm solution of tartaric acid.

C. SOLUTION OF IODIDE OF ANTIMONY IN HYDRIODIC ACID, or ACID HYDRIODATE OF ANTIMONIC OXIDE.—The reddish-yellow liquid formed in the decomposition of teriodide of antimony by water. When 1 part of the teriodide is decomposed by 6 parts of water, the resulting solution contains 6·17 per cent. of antimony and 90·83 of iodine; on further dilution, a reddish-yellow powder is deposited. This compound, when distilled, yields free iodine and a reddish-yellow and subsequently a black distillate, while reddish-brown teriodide of antimony is left in the retort. (Brandes & W. Böttger, *N. Br. Arch.* 17, 283.)

D. IODO-SULPHIDE OF ANTIMONY.—On exposing a dry and intimate mixture (reddish-brown in colour) of equal parts of iodine and sulphide of antimony to a moderate heat in a retort placed in a sand bath, the new compound is evolved in red vapours, and deposited in the form of a sublimate.—The following mixture may also be sublimed: 24 parts of antimony with 9 parts of sulphur and 68 parts of iodine; or 2 parts of antimony with 9 parts of iodide of sulphur; but in this case, crystallized sulphur is likewise mixed with the sublimate.—Brilliant, transparent, blood-red scales and needles, which fuse at a gentle heat, and volatilize in red vapours at a lower temperature than iodide of antimony, and without decomposition. Has an unpleasant odour, and a nauseous, pungent taste.

	Calculation.		Henry & Garot.
Sb	129	23·24	23·2
3S	48	8·65	8·8
3I	378	68·11	66·4
SbS^3,I^3?	555	100·00	98·4

When strongly heated in the air, it is resolved into iodine, sulphur, sulphurous acid, metallic antimony, and antimonic oxide which volatilizes. It dissolves in sulphuric acid, nitric acid, hydrochloric acid, and aqua-regia, with separation of the iodine, and partly also of the sulphur.—Chlorine converts it into chloride of iodine, chloride of sulphur, and chloride of antimony.—Hydrosulphuric acid and sulphurous acid gas do not affect it. —When mixed with water, it is resolved into hydriodic acid which dissolves, and an insoluble orange-yellow mixture of sulphur, antimonic oxide, and a small quantity of iodide of antimony. Solution of ammonia separates hydriodic acid in a similar manner: so likewise do alcohol and ether, excepting that they also dissolve a small quantity of sulphur. The fixed alkalis likewise cause decomposition. (O. Henry & Garot, *J. Pharm.* 10, 511; also *Schw.* 43, 53.)

E. Iodide of Antimony + Sulphide of Antimony.—From a very dilute solution of iodide of antimony in hydrochloric acid, hydrosulphuric acid precipitates a mixture of iodide and sulphide of antimony, from which the iodide of antimony is sublimed by heat. (Johnston, *N. Edinb. Phil. J.* 18, 43.)

Antimony and Bromine.

A. Terbromide of Antimony.—Antimony takes fire when brought in contact with bromine, the metal running about in glowing fused globules on the surface of the bromine. (Balard, Serullas.) Bromide of antimony is prepared in a similar manner to bromide of arsenic (p. 283), but the neck of the retort must be kept hot during the distillation to prevent stoppage.—Colourless mass crystallized in needles, which fuse at 94° and boil 270°.—Absorbs moisture from the air. Water instantly resolves it into hydrobromic acid—which, if a large quantity of water be added, does not retain a trace of antimonic oxide—and basic hydrobromate of antimonic oxide. (Serullas, *Ann. Chim. Phys.* 38, 322; also *Pogg.* 14, 112.) —Cold nitric acid does not decompose terbromide of antimony, but at a boiling heat, resolves it into bromine vapour and a white insoluble powder (nitrate of antimonic oxide); oil of vitriol likewise does not disengage bromine vapour unless aided by heat. (Löwig, *Repert.* 29, 266.)

Calculation, according to Serullas.

Sb	129·0	35·42
3Br	235·2	64·58
$SbBr^3$	364·2	100·00

B. Hydrated Oxy-bromide of Antimony, or Basic Hydrobromate of Antimonic Oxide.—Prepared by decomposing terbromide of antimony by water. When dried at a temperature at which decomposition commences, it still retains water, which, at a higher temperature, is evolved together with terbromide of antimony, while antimonic oxide is left behind. By washing it repeatedly with small quantities of water, the whole of the bromine may be removed. (Serullas.)

Antimony and Chlorine.

A. Terchloride of Antimony.—*Butter of Antimony, Spiessglanzbutter, Butyrum Antimonii, Causticum antimoniale.*—1. Terchloride of antimony is formed by passing chlorine gas over heated sulphide of antimony, and separating the chloride of sulphur, produced simultaneously with the chloride of antimony, by volatilization at a gentle heat. (H. Rose.) —The affinity of the chloride of sulphur for terchloride of antimony prevents the latter from combining with more chlorine, and thereby passing into pentachloride of antimony. (Mitscherlich.)—2. By distilling 3 parts (1 At.) of antimony with 8 parts (nearly 3 At.) of corrosive sublimate. (Basil Valentine.)

$$Sb + 3HgCl = SbCl^3 + 3Hg.$$

If the heat be not kept very moderate, mercury likewise passes over into the receiver.—3. By distilling 2 parts (1 At.) of sulphide of antimony with 5 parts (or better with 4·6 pts. = 3 At.) of corrosive sublimate.

$$SbS^3 + 3HgCl = SbCl^3 + 3HgS. \quad (\textit{Sch.}\ 45.)$$

Towards the end of the process, *Cinnabaris Antimonii* is sublimed.—4. Acid hydrochlorate of antimonic oxide is moderately heated in a retort, till the water and excess of hydrochloric acid are driven off, and the residue has acquired the consistence of butter; the receiver is then changed, and the terchloride of antimony distilled over at a higher heat.—Glauber used for this purpose a solution of flowers of antimony in hydrochloric acid.—Robiquet (*Ann. Chim. Phys.* 4, 165, also *Schw.* 19, 189,) dissolves 1 part of antimony in a mixture of 4 parts of hydrochloric acid and 1 part of nitric acid; the latter must be added in small successive portions, and a gentle heat applied. If too much chlorine is given off on evaporation, the nitric acid is in excess, and an additional quantity of antimony and hydrochloric acid must be added. It is always advisable to have a portion of metallic antimony at the bottom of the retort.—Göbel (*Br. Arch.* 2, 216), treats 1 part of sulphide of antimony with 3 pts. hydrochloric acid of specific gravity 1·2, and $\frac{1}{2}$ pt. nitric acid of specific gravity 1·55—decants the liquid from the sulphur—and distils till half has passed over.—Brandes (*N. Tr.* 3, 1, 261, and *Repert.* 11, 289), treats 1 part of sulphide of antimony with a mixture of 5 pts. of strong hydrochloric and 1 pt. of nitric acid; decants the solution thus obtained; digests the residue in a mixture of $\frac{1}{2}$ pt. hydrochloric and $\frac{1}{9}$ pt. nitric acid; and distils the two liquids together, whereby, after the watery portion has passed over, $1\frac{1}{2}$ pt. butter of antimony is obtained.—Geiger & Reimann (*Mag. Pharm.* 17, 126), gently heat 1 pt. of sulphide of antimony with a mixture of 3 pts. hydrochloric acid, of specific gravity 1·16, and 0·72 pt. nitric acid, of specific gravity 1·171, till the solution, which is at first yellow, becomes colourless, and then decant it. An excess of nitric acid is to be avoided, because it produces antimonic acid on evaporation.—Liebig dissolves 1 pt. of sulphide of antimony in 3 pts. of hot fuming commercial hydrochloric acid; evaporates the decanted solution, till a drop solidifies when placed upon cold metal; and then distils it from a retort, changing the receiver as soon as the distillate solidifies on cooling.—6. By distilling sulphate of antimonic oxide, or some substance capable of producing it, with common salt.

$$SbO^3,3SO^3 + 3NaCl = SbCl^3 + 3(NaO,SO^3).$$

Berzelius evaporates sulphuric acid with antimony or antimonic oxide, and distils the residue with twice its weight of common salt.—A mixture of 1 pt. of roasted sulphide of antimony with 3 pts. of decrepitated common salt is distilled with 1½ pt. of fuming oil of vitriol. (*Crell. Chem. J.* 6, 76.)—Glauber and Becher distil 1 pt. of sulphide of antimony with 2 pts. of common salt and 4 pts. of burnt sulphate of iron. Rolfink uses equal parts.—In distilling butter of antimony, it is necessary to use a wide-necked retort; if, however, it becomes stopped up by the solidification of the compound, the solid mass must be melted by holding a hot coal under it.

Translucent, colourless, solid, crystalline mass, which at 72° (Capitaine), fuses to a colourless or yellowish oil; boils at 197·8° (H. Davy), at 230° (Capitaine); emits scanty white fumes in the air; is very corrosive.

	Calculation.		J. Davy.	Göbell.	H. Rose.
Sb	129·0	54·85	60·42	54·98	53·27
3Cl	106·2	45·15	39·58	45·02	46·73
$SbCl^3$	235·2	100·00	100·00	100·00	100·00

When distilled with an equal weight of sulphur (whereby a small quantity of butter of antimony is volatilized undecomposed), it is resolved into a volatile liquid, [pentachloride of antimony or chloride of sulphur?] which distils over, and grey sulphide of antimony which remains in the retort. (A. Vogel, *Schw.* 21, 70.)—When treated with hot nitric acid, it evolves chlorine gas, and leaves a white powder (antimonic acid).—It is not decomposed by cold oil of vitriol; but when boiled with that liquid, it is resolved into hydrochloric acid gas, and sulphate of antimonic oxide which remains in the form of a white mass. (A. Vogel.)—When heated with sulphocyanide of potassium, it yields vapour of bisulphide of carbon, tetrasulphide of antimony, and mellonide of potassium. (Liebig.)—It gradually absorbs moisture from the air, and deliquesces to a turbid liquid.—100 parts of terchloride of antimony, exposed for 70 days to air saturated with moisture, absorb 110 parts of water, but no more afterwards; during the absorption, the chloride first deliquesces and then deposits a white precipitate. (Brandes, *Schw.* 51, 437.)—It is only when free hydrochloric acid is present, that the chloride deliquesces without turbidity. (H. Rose, *Pogg.* 55, 551.) When small pieces of terchloride of antimony are laid on mercury, they revolve about for some time, till the mercury becomes covered with a film of acid hydrochlorate of antimonic oxide. (Jacquelain, *Ann. Chim. Phys.* 66, 123.)—When chloride of antimony is mixed with a large quantity of water, it is resolved without perceptible rise of temperature, into oxy-chloride of antimony, which is precipitated, and acid hydrochlorate of antimonic oxide, which dissolves.

Terchloride of antimony combines with chloride of sulphur. It does not absorb hydrochloric acid gas.

B. OXY-CHLORIDE OF ANTIMONY.—*Powder of Algaroth, Pulvis Algaroth s. angelicus, Mercurius vitæ.*—This compound is precipitated on adding water to terchloride of antimony or to acid hydrochlorate of antimonic oxide. It may also be obtained by mixing 1 pt. of glass of antimony with 3½ pts. of common salt, 2½ pts. of oil of vitriol, and 2 pts. of water—heating the liquid for 12 hours nearly to the boiling point—diluting the solution with water till a precipitate begins to appear—then filtering, and precipitating with more water. (Scheele, Bucholz.) Instead of common salt and oil of vitriol, strong hydrochloric acid may also be used. Liebig boils strong commercial hydrochloric acid with finely powdered sulphide of antimony to saturation; then adds enough water to precipitate a small quantity of powder of algaroth, whereby the hydrosulphuric acid present in the liquid is carried down in the form of sulphide of antimony; and lastly, filters and precipitates by a further addition of water.

The precipitate is washed with a very small quantity of cold water. When the snow-white bulky precipitate is collected on a filter immediately after its formation, and then washed and dried, it yields a powder; but if it be allowed to stand under the liquid for two or three days, it forms a greyish-white mass, consisting of small prisms. The crystals are dried between folds of bibulous paper; if washed with water, they become dull in consequence of superficial decomposition. (Johnston, *N. Edinb. Phil. J.* 18, 40; also *J. pr. Chem.* 6, 55; Malaguti, *Ann. Chim. Phys.* 59, 220; also *J. pr. Chem.* 6, 253.) ¶ Peligot (*Ann. Chim. Phys.* 3, 20, 283), regards the oxy-chloride obtained by treating butter of antimony with cold water, as $SbClO^2$, and the compound which is deposited in dense brilliant crystals, on boiling terchloride of antimony or hydrochlorate of antimonic oxide with water, and subsequent cooling, as $2SbClO^2$. ¶

White powder, or fine, greyish-white, highly brilliant needles, (Bucholz, *Taschenb.* 1806, 18), which, according to Johnston & Miller, are oblique rectangular prisms, having the obtuse summits replaced by planes.

	Calculation.		Johnston.	Duflos.	Bucholz.	Phillips
6Sb	774·0	77·38	76·82			77·98
3Cl	106·2	10·62	11·25	10·37	10·05	7·80
15O	120·0	12·00				
$SbCl^3,5SbO^3$	1000·2	100·00				

Or :

	Calculation.		Peligot. (1)	Peligot. (2)
2Sb	258·00	77·3	76·5	76·8
Cl	35·41	10·6	11·1	11·4
3O	24·00	12·1		
$2SbClO^3$	317·41	100·0		

Or :

			Malaguti.	Grouvelle.
$SbCl^3$	235·2	76·48	74·51	82
$5SbO^3$	765·0	23·52	25·70	18
	1000·2	100·00	100·21	100

The slight excess of chlorine obtained by Johnston probably arose from not washing the product. (Johnston regards the powder of algaroth as $2SbCl^3+9SbO^3$); Bucholz and Grouvelle (*Schw.* 33, 431), and especially Phillips (*Phil. Mag. Ann.* 8, 406; also *Br. Arch.* 39, 40), found too little chlorine, doubtless from over-washing; Grouvelle's analysis gives the formula $SbCl^3,7SbO^3$.—Powder of algaroth does not lose weight at 100°, and only 0·38 per cent. of water by ignition with dry carbonate of soda. (Johnston.)

Powder of algaroth fuses when strongly heated, and is resolved into terchloride of antimony which distils over, and a residue of antimonic oxide. (Bergman.) The crystals decrepitate during the decomposition. (Johnston.) When the powder is strongly heated in a glass tube, the antimonic oxide likewise volatilizes, so that nothing remains. (H. Rose.)—When ignited with sulphur, it gives off sulphurous acid [and pentachloride of antimony or chloride of sulphur?] and is converted into 110·5 per cent. of grey sulphide of antimony. (Grouvelle.) By boiling with nitric acid it is converted into antimonic oxide. (Bucholz.) By long continued washing with hot water, the whole of the chlorine is removed in the form of hydrochloric acid, and pure antimonic oxide left on the filter. (N. E. Henry, *J. Pharm.* 12, 79; Duflos, *Schw.* 67, 268; Malaguti.) The chlorine is likewise completely removed by aqueous solutions of the alkaline carbonates.

When powder of algaroth is precipitated from a liquid containing hydrosulphuric acid,—*e. g*, from a solution of grey sulphide of antimony in strong hydrochloric acid, by diluting with water after decantation—it forms a bulky yellowish precipitate, which aggregates in red crystals, if kept under the liquid for a few days. These crystals consist of powder of algaroth mixed with a variable quantity, at most 2 per cent., of sulphide of antimony. (Malaguti.)

C. Solution of Hydrochlorate of Terchloride of Antimony or Acid Hydrochlorate of Antimonic Oxide.—*Liquor Stibii muriatici* of the *Pharmac. Bor.*—1. Prepared by decomposing terchloride of antimony with a small quantity of water, and decanting the liquid from the powder of algaroth thereby produced. This solution is the old *Spiritus Vitrioli philosophicus*.—2. By dissolving terchloride of antimony in aqueous hydrochloric acid; the solution being effected without any precipitation.—3. By dissolving sulphide of antimony in strong boiling hydrochloric acid.—4. By dissolving antimonic oxide, glass of antimony, or crocus of antimony, in strong hydrochloric acid, and decanting or distilling the liquid.—5. By the same process as that given for the preparation of terchloride of antimony under (5), either without distilling the resulting solution, or distilling it without changing the receiver, so that the aqueous hydrochloric acid which first passes over, may mix with the subsequent distillate of terchloride of antimony.—6. By distilling a mixture of glass of antimony, crocus antimonii, or sulphide of antimony, with common salt and dilute sulphuric acid, the retort being heated nearly to redness towards the end of the process; *e. g.* 1 pt. of glass of antimony, 4 pts. of common salt, 3 pts. of oil of vitriol, and 2 pts. of water, (Göttling);—1 pt. of crocus of antimony, 3 pts. of common salt, 2 pts. of oil of vitriol, and 1 pt. of water (*Pharmac. Boruss.*, edit. 3);—2 pts. of grey sulphide of antimony, 3 pts. of common salt, 2 pts. of oil of vitriol, and 2 pts of water. The hydrosulphuric acid which passes over, re-precipitates a small quantity of sulphide of antimony from the distillate.—7. By distilling to dryness a mixture of 8 pts. of antimony, 14 pts. of common salt, 5 pts. of peroxide of manganese, 12 pts. of oil of vitriol, and 12 pts. of water. (Brandes.)

Yellowish liquid, of specific gravity, 1·35....1·50; fumes when concentrated, and when considerably diluted, deposits a large quantity of powder of algaroth.

D. Solution of Acid Hydrochlorate of Antimonious Acid.—The hydrate of antimonious acid dissolves sparingly in strong hydrochloric acid. The pale yellow solution is precipitated white by water, after a short time; with a large excess of water, however, no precipitation takes place.

E. Pentachloride of Antimony.—Powdered antimony takes fire in chlorine gas at ordinary temperatures, and burns with a reddish white light and emission of sparks, forming pentachloride of antimony. Terchloride of antimony is never formed in this manner. (H. Rose.)—Terchloride of antimony absorbs chlorine gas, till it is converted into the pentachloride. (Liebig.)—The pentachloride may be prepared by passing dry chlorine gas over powdered antimony gently heated. *App.* 45 may be used for the preparation, excepting that a tubulated retort, containing antimony and provided with a receiver, must be substituted for *d.*—Liebig passes chlorine gas, dried by means of oil of vitriol, over terchloride of antimony.—Colourless, or very pale yellow, mobile liquid, specifically heavier than water, very volatile, fumes strongly in the air, and has a sharp acid odour.

	Calculation.			H. Rose.
Sb	129	42·16		40·56
5Cl	177	57·84		59·44
$SbCl^5$	306	100·00		100·00

Pentachloride of antimony when heated gives off chlorine gas, together with a small quantity of undecomposed pentachloride, and leaves a residue of terchloride of antimony. The liquid, supersaturated with chlorine, begins to boil at 24°; gives off the first drops of pentachloride of antimony at 140°; and leaves a residue of terchloride of antimony at 200°: the pentachloride of antimony which passes over may be further decomposed by a second distillation. (Mitscherlich.) Pentachloride of antimony gives up chlorine to a few organic compounds—olefiant gas for example—and is thereby converted into the terchloride. When exposed to the air, it absorbs moisture, and is converted into a white crystalline mass of hydrated pentachloride of antimony, or crystallized hydrochlorate of antimonic acid; with a larger quantity of water, considerable heat is disengaged, and the pentachloride is resolved into insoluble hydrate of antimonic acid and aqueous hydrochloric acid, which retains only a small quantity of antimonic acid in solution. (H. Rose.)

Hydrated Pentachloride of Antimony or *Crystallized Hydrochlorate of Antimonic Acid.*—This compound forms colourless, transparent, rhombic prisms, with dihedral summits resting on the obtuse lateral edges. *Fig.* 63, without the *p*-face. The crystals deliquesce in the air without becoming milky; but a larger quantity of water precipitates antimonic acid.

Solution of Acid Hydrochlorate of Antimonic Acid.—When hydrate of antimonic acid is treated with hot concentrated hydrochloric acid, a yellowish solution is obtained, which becomes cloudy after a while when mixed with a small quantity of water, but remains perfectly clear if treated at once with a large excess.

F. Pentachloride of Antimony with Phosphuretted Hydrogen.—When pentachloride of antimony is treated with phosphuretted hydrogen, the gas is absorbed—a small quantity of hydrochloric acid is evolved—and a red solid substance formed, which, with ammonia, yields spontaneously inflammable phosphuretted hydrogen, but with water and other aqueous solutions, the non-spontaneously inflammable variety of that compound. (H. Rose, *Pogg.* 24, 165.)

G. Bichloride of Sulphur with Pentasulphide of Antimony.—Grey sulphide of antimony is not affected by a current of chlorine gas at ordinary temperatures; but if the sulphide be gently heated at one point only, it is completely converted, first into a brown liquid, and then, after absorbing more chlorine, into a white powder. To prevent the decomposition of the new compound by the heat evolved during the absorption of chlorine, the tube is kept cool by moistening it with alcohol or ether. 177 parts of sulphide of antimony yield 493·2 parts of the compound; the calculated quantity is 566·4 parts; but portions of chloride of sulphur and chloride of antimony are volatilized by the heat, and the pentachloride gives off chlorine and is thereby partially converted into terchloride. (H. Rose.)

White, amorphous powder. When heated, it fuses, evolves chloride of sulphur and free chlorine, and leaves terchloride of antimony. Dissolves in very dilute nitric acid, with evolution of nitrous acid fumes, but without any separation of antimonic acid or antimonic oxide. Water resolves it into hydrochloric acid, antimonic acid, sulphuric acid, and hyposulphurous acid. It absorbs a quantity of ammoniacal gas, amounting to $\frac{2}{3}$ of the sulphide of antimony used. (H. Rose, *Pogg.* 42, 532.)

	Calculation.			H. Rose.
Sb	129·0	....	22·77	25·67
3S	48·0	....	8·48	7·63
11Cl	389·4	....	68·75	66·70
$SbCl^5, 3SbCl^2$	566·4	....	100·00	100·00

The want of accordance between the analysis and the calculation is explained by the sources of error mentioned in the preparation.

H. Tersulphide of Antimony with Terchloride of Antimony.—By passing hydrosulphuric acid gas through acid hydrochlorate of antimonic oxide, a bright yellowish red precipitate is formed, which retains chloride of antimony, however long it may be washed. The compound blackens even after several hours' drying in a water bath, and evolves chloride of antimony; when heated more strongly in a retort, it gives off liquid acid hydrochlorate of antimonic oxide,—probably from containing hygroscopic water,—and a small quantity of hydrosulphuric acid, leaving 90·08 per cent. of tersulphide of antimony. (Gmelin.) Even when the hydrosulphuric acid gas is in excess, the precipitate contains terchloride of antimony, which is evolved on heating. (Johnston, *N. Edinb. Phil. J.* 18, 43.) According to H. Rose, the sulphide of antimony is precipitated free from chloride, if tartaric acid is added to the acid hydrochlorate of antimonic oxide before treating it with hydrosulphuric acid gas. The precipitate thus obtained has a deeper brown-red colour, and, according to the author's experiments, contains, after thorough washing, only a trace of terchloride of antimony. Duflos (*Schw.* 67, 271) found that it still retained considerable quantities of terchloride, amounting to between $\frac{1}{10}$ and $\frac{1}{20}$ of the precipitate, according to the mode of preparation; that only part could be extracted by repeated boiling with water; and moreover, that it was not decomposed by passing a current of hydrosulphuric acid through water in which it was diffused; but, on the contrary, that bihydrosulphate of potash decomposed it completely, so that pure kermes was left behind and partly dissolved.

Tersulphide of antimony dissolves abundantly in boiling hot acid hydrochlorate of antimonic oxide, and the solution deposits yellow and red crystals on cooling. (Liebig.)

Antimony and Fluorine.

A. Terfluoride of Antimony.—Prepared by distilling powdered antimony with fluoride of mercury. At ordinary temperatures, solid and snow-white; more easily volatilized than oil of vitriol, but less easily than water. (Dumas, *Ann. Chim. Phys.* 31, 435.) Crystallizes, by slow evaporation from the aqueous solution, in colourless crystals. Has the taste of tartar-emetic. Very soluble in water, in which it dissolves without the slightest decomposition. (Berzelius, *Pogg.* 1, 34.)

B. and C. Tetrafluoride and Pentafluoride of Antimony.—These compounds are very soluble in water and combine with other metallic fluorides, forming double salts which have not been further examined. (Berzelius.)

Antimony and Nitrogen.

A. Nitrate of Antimonic Oxide, Antimonic Nitrate.—Antimony is oxidized by strong nitric acid, even at ordinary temperatures, but by dilute nitric acid only with the aid of heat; in this process, water is likewise decomposed at the same time and nitrate of ammonia produced; the excess of acid retains but a small quantity of antimonic oxide in solution, and deposits small crystals [on cooling?]. The remaining oxide combines with a certain portion of nitric acid, forming a white crystalline powder, which is likewise obtained on treating the oxide with nitric acid. The same salt is formed by heating antimonic oxide with nitric acid—¶ or, according to Peligot, by dissolving the oxide in cold fuming nitric acid, and adding water to the solution, whereby it is obtained in crystals having a mother-of-pearl lustre. ¶—According to Bucholz, it contains 84⅔ per cent. of antimonic oxide and 15⅓ of nitric acid. When gently heated, it is converted into antimonic acid, which however is reduced to antimonious acid by ignition. It gives up the whole of its acid, even to cold water, after long continued digestion, and leaves pure antimonic oxide. (Bucholz, *Taschenb.* 1806, 89, Berzelius.) Its formula is $2SbO^3,NO^5$. (Peligot.)

Neither antimonious acid (Berzelius) nor antimonic acid is soluble in nitric acid. (H. Rose.)

B. Compound of Antimonic Oxide and Ammonia.—Prepared by treating oxy-chloride of antimony with solution of ammonia. White or greyish-white granular powder, sparingly soluble in water. (Berzelius.)

C. ANTIMONITE OF AMMONIA.—The aqueous solution gives off ammonia when exposed to the air and deposits a white powder consisting of *Acid Antimonite of Ammonia.* (Berzelius.)

D. ANTIMONIATE OF AMMONIA.—¶ *a. Bibasic (Meta-)antimoniate.*—Obtained according to Fremy (*Ann. Chim. Phys.* 3, 23, 411), by leaving hydrated meta-antimonic acid (p. 331) in contact with strong solution of ammonia for several weeks. The acid dissolves slowly, forming a salt which is difficult of isolation, and contains 2 atoms of ammonia with 1 atom of the acid, corresponding to the bibasic potash-salt. ¶

b. Mono-antimoniate.—1. The hydrate of antimonic acid dissolves in warm solution of ammonia; but on evaporating the solution, *Acid Antimoniate of Ammonia* is deposited, in the form of a white powder which reddens litmus, and, when strongly heated, evolves the rest of the ammonia together with water, leaving pure antimonic acid. (Berzelius.) ¶—2. *α. With 6 Atoms of Water* (Fremy's *Mono-meta-antimoniate*).—Precipitated in the crystalline form on adding a few drops of alcohol to a solution of the bibasic salt. Very instable. [This salt forms a good test for soda, which it precipitates almost completely.]

	Calculation, *α*.				Fremy.
NH^3	17	....	6·83		
SbO^5	169	....	67·87	....	67·1
$7HO$	63	....	25·30		
$NH^4O,SbO^5 + 6Aq$	249	....	100·00		

β. With 4 Atoms of Water.—Fremy's *Ordinary Antimoniate.*—The crystalline salt *α* passes into this variety spontaneously and at ordinary temperatures in the course of a few days, even when preserved in closely stopped bottles; the change is marked by the crystals becoming slightly moist and mealy, after which they are no longer soluble in water.—2. The salt *α* when boiled with water loses its crystalline aspect and is converted into a white insoluble powder, without any loss of ammonia.—3. When either antimonic or meta-antimonic acid is dissolved in warm solution of ammonia, this salt always separates on cooling. Moreover, if too great an excess of ammonia is used in the preparation of *α*, a large quantity of the insoluble variety appears likewise to be formed. (Fremy.) ¶

	β, dried in vacuo.				Fremy.
NH^3	17	....	7·3		
SbO^5	169	....	73·2	....	74·0
$5HO$	45	....	19·5		
$NH^4O,SbO^5 + 4Aq.$	231	....	100·0		

E. SULPHANTIMONIATE OF AMMONIUM.—A compound of *Pentasulphide of Antimony* with *Hydrosulphate of Ammonia.*—1. Obtained by digesting an excess of pentasulphide of antimony with the aqueous solution of hydrosulphate of ammonia, and heating the mixture nearly to the boiling point. The pentasulphide may likewise be digested with ammonia, but in that case, a white powder [antimoniate of ammonia?] is separated and the solution is less pure. The yellow solution may be evaporated without decomposition. Acids decompose it, precipitating the pentasulphide of antimony; it is also decomposed by alcohol,—but then the pentasulphide contains ammonia. By decomposing the solution with hydrochloric acid, 209 parts (1 At.) of precipitated pentasulphide of antimony are obtained to 199 parts (rather more than 3 At.) of sal-ammoniac;—hence the solution contains $3NH^4S,SbS^5$. (Rammelsberg, *Pogg.* 52, 214.)

It is moreover probable that the following compound has a similar composition, though Kohl regarded it as consisting of hydrosulphate of ammonia and tersulphide of antimony. It is thus prepared: recently precipitated and still moist tersulphide of antimony is digested in a covered vessel with excess of a concentrated solution of monohydrosulphate of ammonia, the solution filtered after cooling, and the filtrate mixed with three times its volume of absolute alcohol. The compound is hereby completely precipitated in the form of a white, sometimes crystalline, sometimes curdy precipitate, the excess of hydrosulphate of ammonia being retained in the liquid. In order to obtain it perfectly crystalline, it is heated with the supernatant liquid till it dissolves—for which purpose, the addition of a small quantity of water is often necessary,—and then set aside to crystallize on cooling. The hydrosulphate of ammonia must be in considerable excess, otherwise the alcohol separates a portion of it from the compound, which then appears yellowish-red. The crystals can only be preserved from decomposition by keeping them under the mother-liquid in a perfectly air-tight vessel. Light yellow rhombohedrons, having a pungent, hepatic, and nauseous metallic taste. They contain 43·05 per cent. of hydrosulphate of ammonia and 56·95 of sulphide of antimony. [This would lead to the formula $4NH^4S,SbS^3$, which is not altogether probable.] When distilled, the salt evolves hydrosulphate of ammonia and sulphur, and leaves grey sulphide of antimony. When exposed to the air, it evolves hydrosulphate of ammonia and turns brown, the rapidity of the change increasing with the warmth and moisture of the atmosphere. The salt dissolves in cold water free from air, and forms a colourless solution; hot water, on the contrary, decomposes it immediately, so that the solution cannot be evaporated without suffering decomposition. Carbonic acid and other acids precipitate kermes from the solution; so likewise do alcohol and ether, which extract the hydrosulphate of ammonia. Alkaline bicarbonates precipitate the kermes after some time only, and the monocarbonates still less readily. (Kohl, *N. Br. Arch.* 17, 267.)

F. AMMONIO-TERCHLORIDE OF ANTIMONY.—Terchloride of antimony absorbs ammoniacal gas. (Grouvelle.) The solid terchloride absorbs the gas but slowly; but if it be fused at a gentle heat in ammoniacal gas and suffered to cool in it, large quantities are absorbed. The compound when heated, gives off the whole of its ammonia, so that pure terchloride of antimony alone remains. It does not deliquesce readily in the air, even after long exposure. (H. Rose.)

	Calculation.		H. Rose.
NH^3	17·0	6·74	7·57
$SbCl^3$	235·2	93·26	92·43
$NH^3,SbCl^3$	252·2	100·00	100·00

G. AMMONIO-PENTACHLORIDE OF ANTIMONY.—Pentachloride of antimony absorbs dry ammoniacal gas with considerable disengagement of heat, and is converted into a brown substance, which turns white when gently heated, and at a higher temperature, sublimes without decomposition, provided it be kept out of contact of air. The sublimate is also white. (H. Rose, *Pogg.* 24, 165.) The elements of this compound are in such proportion, that, when decomposed by water, the products are monohydrochlorate and antimoniate of ammonia. (Persoz, *Ann. Chim. Phys.* 44, 322.)

$$6NH^3,SbCl^5 + 5HO = 5(NH^3,HCl) + NH^3,SbO^5.$$

	Calculation.		Persoz.
$6NH^3$	102	25	26·05
$SbCl^5$	306	75	73·95
$6NH^3,SbCl^5$	408	100	100·00

H. COMPOUND OF TERCHLORIDE OF ANTIMONY AND SAL-AMMONIAC.—A solution of 235·2 parts (1 At.) of terchloride of antimony and 106·8 parts (2 At.) of sal-ammoniac, yields double six-sided pyramids. (Jacquelain, *Ann. Chim. Phys.* 66, 128.)—Antimonic oxide dissolves in a cold solution of sal-ammoniac. (Brett, *Phil. Mag. J.* 10, 97.)

	Crystallized.		Or:			Jacquelain.
$2NH^4Cl$	106·8	31·23	$2NH^4$	36	10·53	
$SbCl^3$	235·2	68·77	Sb	129	37·72	37·5
			5Cl	177	51·75	50·8
$2NH^4Cl,SbCl^3$	342·0	100·00		342	100·00	

¶ According to Poggiale (*Compt. rend.* 20, 1180, also *Ann. Pharm.* 56, 243), when terchloride of antimony is poured into a solution of sal-ammoniac, a slight cloudiness only is produced, and the mixture yields, on gentle evaporation, rectangular prisms composed of $3NH^4Cl + SbCl^3 + 3Aq$.—On further evaporating the mother-liquid, cubes or pyramidal cubes are deposited, the formula of which is $2NH^4Cl + SbCl^3 + 2Aq$.—Both these compounds are colourless and transparent, but become yellow and opaque on exposure to the air; moreover, they are decomposed by a large quantity of water. ¶

ANTIMONY AND POTASSIUM.

A. ANTIMONIDE OF POTASSIUM.—1. Four parts of powdered antimony combine readily with 1 part of potassium, the union being attended with incandescence. (Gay-Lussac & Thénard.)—2. The same compound, containing about 5 per cent. of potassium, is formed by heating a mixture of equal parts of antimony or roasted sulphide of antimony, and cream of tartar, to strong redness in a covered crucible for about two hours. (Vauquelin.)—3. By igniting a mixture of 12 parts of antimony with 10 parts of carbonate of potash and 2 parts of charcoal. With a larger proportion of charcoal, a black pyrophoric mass is produced. (Serullas.)—4. Tartar-emetic which has been first roasted in the air till it has appeared incandescent, and then been powdered, is ignited alone,—or unroasted tartar-emetic is ignited with $\frac{1}{10}$ its weight of nitre. The alloy in this case is very rich in potassium; when unroasted tartar-emetic is ignited by itself, it yields a black pyrophoric mass. (Serullas.)—The alloy must be preserved in well-closed bottles under rock-oil.—Greyish-white, soft, brittle, having a fine-grained fracture; rather fusible. The compound obtained by method (4) contains a larger amount of potassium; it may be beaten out in laminæ, and gives off numerous sparks under the hammer.—Oxidizes rapidly in the air, and, when in powder, disengages so much heat that it sets fire to paper.—Under water it rapidly evolves hydrogen gas.—When the antimony contains arsenic, the hydrogen is mixed with arseniuretted hydrogen gas.—The compound richer in potassium revolves rapidly when placed on mercury moistened with water (I., 381; Gay-Lussac & Thénard; Vauquelin, *Ann. Chim. Phys.* 7, 32; Serullas, *J. Phys.* 91, 123.)

B. COMPOUND OF ANTIMONIC OXIDE WITH POTASH.—When oxychloride of antimony is digested with solution of potash, it is converted into a greyish-white granular powder, which is but sparingly soluble in water; the supernatant liquid contains a small quantity of antimonic oxide. The powder is slightly dissolved by the potash on boiling, and separates again as the liquid cools (Berzelius) [in small, brilliant, colourless and transparent crystals].—Pure antimonic oxide yields the same compound with solution of potash. After repeated washing, whereby potash is separated, it still contains 6·35 per cent. of potash to 93·65 of antimonic oxide; after this it does not give up any more potash to boiling water, but dissolves without decomposition in 425 parts of hot water. (Brandes, *Schw.* 62, 199.)—This compound dissolves less abundantly in strong than in dilute caustic potash. The solution is rapidly converted in the air into a solution of carbonate of potash, while antimonite of potash crystallizes out. When ignited with carbonate of potash, the antimonic oxide expels the carbonic acid, and if in excess, forms an easily fusible compound; with an excess of carbonate of potash, on the contrary, the mass is less fusible, and is resolved into metallic antimony and antimonite of potash. (Liebig.)—The recently precipitated oxide dissolves abundantly in aqueous solution of potash, and in still larger proportion in carbonate of potash; but if it be treated with a quantity of potash smaller than that which is required for solution, a small portion only is taken up; after prolonged washing with water, the oxide retains only 1 per cent. of potash. When antimonic oxide is fused with carbonate of potash, and the resulting mass is exhausted with water, the antimonic oxide which remains undissolved, retains a somewhat larger quantity, but not in any simple stoïchiometrical proportion. (H. Rose & Varrentrapp, *Pogg.* 47, 326.)

C. ANTIMONITE OF POTASH.—*a. Mono-antimonite.*—Prepared by fusing antimonious acid with excess of hydrate or carbonate of potash, removing the excess of alkali with cold water, and then treating the residue with boiling water. The latter solution does not crystallize on evaporation, but dries up to a yellowish saline mass, which has an alkaline and metallic taste, and is perfectly soluble in water (very sparingly in water containing potash). The solution, when treated with carbonic acid, even in small quantity, deposits the salt *b*.

b. Bi-antimonite.—White powder, from which stronger acids extract the whole of the potash. (Berzelius.)

	At.		*a.*	Berzelius.
KO	1	47·2	22·67	23·37
SbO^4	1	161·0	77·33	76·63
KO,SbO^4	1	208·2	100·00	100·00

	At.		*b*, according to Berzelius.
KO	1	47·2	12·78
SbO^4	2	322·0	87·22
$KO,2SbO^4$	1	369·2	100·00

¶ Fremy (*Ann. Chim. Phys.* 3, 12, 498) denies the existence of these salts, and regards the mass obtained by fusing the so-called antimonious acid with potash, as antimoniate of potash, mixed more or less with the compound of antimonic oxide and potash. ¶

D. Antimoniate of Potash.—¶ *a. Bibasic Antimoniate.*—Fremy's *Neutral Meta-antimoniate.*—$2KO,SbO^5$. When a mixture of 1 part of antimonic acid and 3 parts of potash is fused in a silver crucible, a mass is obtained, which is completely soluble in water containing potash; and the solution, on being slowly evaporated, deposits rounded crystals of this salt. The crystals are purified with difficulty, because water decomposes them; they are very deliquescent. According to Fremy, the proportion between the base and the acid is (1) as 1 : 1·729; (2) as 1 : 1·63; the proportion calculated from the formula is as 1 : 1·78. Hence it may be considered bibasic. When the salt is boiled for some time with water, and the solution evaporated, gummy antimoniate of potash, *b*, γ, is deposited after a short time, and free potash found in the liquid. But if the salt is treated with cold water, it is resolved into free potash, and sparingly soluble, granular antimoniate, or acid meta-antimoniate of potash, *b*, δ. (E. Fremy, *N. Ann. Chim. Phys.* 12; 502; 23, 408.)

b. Monobasic antimoniate.—α. *Monohydrate.*—Obtained by exposing the hydrate with 7 atoms of water to a temperature of 200°.

β. *Terhydrate.*—Formed when the pentahydrate is heated to 160° for several hours. Perfectly insoluble in cold water; by long continued boiling with water, it recombines with 2 atoms of water, and is reconverted into the gummy pentahydrate. ¶

γ. *Pentahydrate.*—This salt is obtained by detonating a mixture of 1 part of antimony or sulphide of antimony with 6 parts of nitre, and washing the resulting mass with cold water; after this, boiling water extracts the salt. When the solution—which is colourless and has a faintly metallic but not alkaline taste, and a scarcely perceptible alkaline reaction—is evaporated to the consistence of honey, it becomes covered with a film consisting of small crystalline grains, and on cooling solidifies to a white saline mass; if the evaporation be continued, it dries up to a transparent fissured mass, which has a honey-yellow colour, but when perfectly dry, appears white and opaque. The dry salt dissolves slowly in cold but readily in hot water. From the hot solution, carbonic acid and the stronger acids, when not added in excess, precipitate the salt *c*. (Berzelius.) Hydrosulphuric acid gas passed through the aqueous solution precipitates $\frac{2}{3}$ of the antimonic acid in the form of pentasulphide of antimony, while the compound $3KS,SbS^5$ remains dissolved. (Rammelsberg.)

	Anhydrous.		Berzelius.
KO	47·2	21·83	20·8
SbO^5	169·0	78·17	79·2
KO,SbO^5	216·2	100·00	100·0

	Crystalline grains.		Rammelsberg.
KO	47·2	18·07	17·29
SbO^5	169·0	64·70	66·15
5HO	45·0	17·23	17·17
+ 5Aq.	261·2	100·00	100·61

¶ According to Fremy, the aqueous solution above mentioned, contains a mixture of different salts, but chiefly the gummy and the insoluble variety. The pentahydrate is soluble in water; gives precipitates with several soluble salts, *e. g.*, with chloride of ammonium; the solution dissolves the insoluble anhydrous salt with facility, and the liquid is then precipitated by all the soluble salts, including those of potash.

δ. With 7 Atoms of Water.—Fremy's *Acid Meta-antimoniate.*—This salt, according to Fremy, is the best adapted for precipitating soda, and is prepared in the following manner:—a mixture of 1 part of antimony and 4 parts of nitre is heated to redness in an earthen crucible, whereby insoluble anhydrous antimoniate of potash is formed; the mass is then washed with cold water to separate the nitrite and nitrate of potash, and boiled with water for two or three hours to convert it into the gummy, soluble antimoniate, the water being replaced as it evaporates. The mass is hereby nearly all dissolved, a small quantity only of biantimoniate of potash being separated. The liquid is then rendered strongly alkaline by the addition of alcoholic solution of potash, and evaporated till a few drops taken out crystallize on cooling. The evaporation is then stopped, whereupon the meta-antimoniate separates in abundance; the alkaline liquid is afterwards decanted, and the salt dried on plates of baked porcelain. The salt invariably contains an excess of alkali; hence it should always be washed two or three times with water before use; and since it is decomposed by long contact with water—first passing into the gummy variety, and then depositing insoluble bi-antimoniate—it should be preserved in the dry state, and dissolved just before use. This salt is characterized by giving an instantaneous crystalline precipitate with salts of soda, and not affecting the dilute solution of an ammoniacal salt. (Fremy.) ¶

			Fremy.	
		δ.	(1)	(2)
KO	47·2	16·91	16·6	78·0
SbO^5	169·0	60·53	61·0	
7HO	63·0	22·56	21·6	22·0
$KO,SbO^5 + 7Aq.$	279·2	100·00	99·2	100·0

c. Bi-antimoniate.—*Antimonium diaphoreticum ablutum*, *Cerussa Antimonii*, *Calx Antimonii alba.*—1. Prepared by mixing antimony or sulphide of antimony with excess of nitre, and projecting the mixture into a red hot crucible by small portions at a time; igniting the mass for some time after the detonation has ceased; and then exhausting with water, which removes nitrate, nitrite, and mono-antimoniate of potash (and likewise sulphate, when sulphide of antimony has been used, and arseniate of potash if any arsenic were present), and leaves the salt *b*.—As thus obtained, it is contaminated with the oxides of lead, iron, and copper, when those metals are present in the antimony used; and also with a quantity of the compound of antimonic oxide and potash, (separable by acetic acid), the amount of which is greater, the smaller the proportion of nitre in the mixture, and the shorter the time of ignition. (O. Figuier.)—2. A mixture of 1 part of antimony purified by Liebig's method (p. 320) with 3 parts of nitre is detonated; the crucible kept at a red heat for an hour and a half; the mass when cold reduced to powder and diffused in 4 parts of water; the clear liquid decanted; the residue boiled with 3 or 4 parts of water; the insoluble portion, which consists of impure salt *b*, washed with boiling water; and the resulting solutions, which contain the salt *a*, treated with a current of carbonic acid gas: an additional quantity of the salt *b* is then obtained, perfectly pure and white. (O. Figuier, *J. Pharm.* 25, 92; also *Ann. Pharm.* 30, 238.)—Instead of carbonic acid, acetic acid may be used, the acid being added in such quantity that the solution may still have a feebly alkaline reaction (Buchner); with the slightest excess of acetic acid, the antimonic acid is precipitated nearly free from potash. (Figuier.)—The preparation of the *Pharm. Bor.*—which recommends boiling the mass obtained by igniting the mixture of antimony and nitre with water and excess of sulphuric acid—is merely hydrate of antimonic acid.—Moreover, by boiling antimonic acid to dryness with a large excess of solution of potash, and igniting, a mass is obtained which leaves a small quantity of bi-antimoniate of potash undissolved, on treating it with boiling water. (Buchner, *Repert.* 66, 168.) When antimonic acid is boiled with solution of potash, it combines with a portion of the potash, but does not dissolve completely, even with a large excess of potash and water. (H. Rose, *Anal. Chem.*)—White powder.

		Ignited.	Berzelius.
KO	47·2	12·26	10·2
$2SbO^5$	338·0	87·74	89·8
$KO,2SbO^5$	385·2	100·00	100·0

		Unignited.	Guibourt.
KO	47·2	10·75	10·97
$2SbO^5$	338·0	76·96	76·73
6HO	54·0	12·29	12·30
+ 6Aq.	439·2	100·00	100·00

E. Sulphantimonite of Potassium.—*Liver of Antimony, Hepar Antimonii.*—Protosulphide of potassium may be fused in all proportions with tersulphide of antimony. These compounds may be obtained by igniting sesquisulphide of antimony with sulphate of potash and charcoal, or with carbonate of potash and charcoal—*e.g.*, the slag formed in the preparation of antimony with black flux (p. 318, 2),—or simply with carbonate of potash, whereby the compound of antimonic oxide and potash (or if the sulphide of antimony predominates, oxy-sulphide of antimony,) is produced at the same time. (*Vid.* p. 375.)

a. A mixture of 177 parts (1 At.) of grey sulphide of antimony, with 485 parts (about 9 At.) of protosulphide of potassium, yields by fusion, a liver of antimony, which, after being poured out of the crucible, flies in pieces on cooling; it also yields a greyish-yellow powder. (Kohl.)

b. By treating sulphide of antimony with excess of carbonate of potash, a compound of 1 atom of tersulphide of antimony with 2 atoms of protosulphide of potassium is formed, besides the compound of antimonic oxide and potash. (Berzelius.)

$$7(KO,CO^2) + 5SbS^3 = 3(2KS,SbS^3) + KO,2SbO^3 + 7CO^2.$$

c. By fusing 3 parts of carbonate of potash with 8 parts of sulphide of antimony, a compound is produced, containing 1 atom of tersulphide of antimony with 1 atom of protosulphide of potassium, having the form of a liver-brown, easily fusible mass. (*Berzelius.*)

$$7(KO,CO^2) + 8SbS^3 = 6(KS,SbS^3) + KO,2SbO^3 + 7CO^2.$$

d. One part of carbonate of potash yields with 16 parts of sulphide of antimony a steel-grey, brittle mass, having a conchoidal, non-crystalline, metallic-shining fracture, and yielding a dark-brown powder. (Berzelius.)—In this case, besides *Regulus antimonii medicinalis* (p. 359), there is also formed a compound of sulphide of potassium with a large excess of sulphide of antimony.

All livers of antimony are brown, fuse easily, and when poured on a flat surface, contract strongly, decrepitating and flying asunder as they cool, (*Vid.* Marx, *Schw.* 59, 251.)—When they are strongly ignited out of contact of air, metallic antimony is separated, and the liver of antimony is partly converted into a compound of protosulphide of potassium with pentasulphide of antimony, so that, on dissolving the mass in water and treating it with an acid, kermes is precipitated at first, and then the lighter-coloured pentasulphide of antimony. (H. Rose.)—When ignited in the air, they burn with formation of white fumes. They colour the skin brown (from containing *crocus antimonii*), rapidly attract moisture from the air, and are resolved by water into soluble sulphide of potassium (which then dissolves a portion of the sulphide of antimony), and an insoluble residue of sulphide of antimony, mixed either with oxy-sulphide of antimony, or the compound of antimonic oxide and potash. According to Kohl, the compound *a*, which is rich in sulphide of potassium, is the only variety which dissolves almost completely.

Solution of Sulphantimonite of Potassium, or *Hydrosulphate of Antimonic Oxide and Potash.*—1. Obtained by dissolving liver of antimony in water.—2. By dissolving sulphide of antimony or antimonic oxide in solution of hydrosulphate of potash.—If bihydrosulphate of potash is used, hydrosulphuric acid gas is evolved; 1 At. of the hydrosulphate does not dissolve so much as ⅛ At. of sulphide of antimony. (Berzelius.) By saturating a hot aqueous solution of hydrosulphate of potash with kermes, a compound of 177 parts (1 At.) of sulphide of antimony with 485 parts (9 At.) of protosulphide of potassium remains dissolved after cooling. (Kohl.)—3. By dissolving sulphide of antimony in boiling solution of potash. The compound of antimonic oxide and potash is hereby formed at the same time. (p. 375.)—The more concentrated and the hotter the alkaline solution, the greater is the quantity of sulphide of antimony dissolved; and on diluting or cooling the liquid, a portion of the sulphide is precipitated, and sometimes forms a gelatinous mass. An excess of free potash, however, prevents the precipitation on cooling. (Berzelius.)—The solution when exposed to the air, deposits kermes, and is partially converted into a solution of sulphantimoniate of potassium. (Berzelius.) [The deposition of kermes is caused by the carbonic acid in the air; the formation of the sulphantimoniate of potassium arises from a portion of the potassium being oxidized by the air, and the sulphur, hitherto combined with it, passing over to the tersulphide of antimony.]

When the slightly yellow solution of the liver of antimony (*a*) in water, or of kermes in aqueous sulphide of potassium, is evaporated to a syrupy consistence, it yields colourless and transparent rhombic laminæ, and flattened needles, arranged in stellated masses, which may be dried by exposure to gentle heat in a vessel containing chloride of calcium. The crystals have a nauseous, bitter, alkaline, and hepatic taste; when strongly heated they lose water, and become opaque, and are converted into brown liver of antimony, which redissolves in water, merely producing a slight turbidity in the liquid.—They dissolve in hydrochloric acid, forming a nearly transparent liquid. With water, they yield a colourless solution, which is decomposed by acids including the carbonic, and also by bicarbonate of ammonia, potash, or soda, hydrosulphuric acid being set free, and yellowish-red sulphide of antimony precipitated; monocarbonate of potash or soda, on the contrary, produces a precipitate of the colour of kermes. Even by exposure to the air, amorphous sulphide of antimony is precipitated. By boiling the solution with an additional quantity of kermes, so large a portion is taken up, that the liquid solidifies in a brown magma on cooling. Absolute alcohol does not dissolve the crystals, but precipitates a portion of the salt in oily drops from the aqueous solution; hydrated alcohol dissolves a quantity proportional to the amount of water which it contains. (Kohl, *N. Br. Arch.* 17, 259.)—It yet remains to be determined whether these crystals are not hydrated sulphantimoniate of potassium.

F. Sulphantimoniate of Potassium.—This compound is likewise a kind of *Liver of Antimony.*—1. It is prepared by a method similar to that used in the preparation of sulphantimonite of potassium, but with the addition of a sufficient quantity of sulphur, previous to fusion.—2. By fusing tersulphide of antimony with a mixture of bisulphate of potash and charcoal.—3. Or by fusing the same compound with tersulphide, tetrasulphide, or pentasulphide of potassium.—4. By exposing sulphantimonite of potassium to a strong red heat, whereby antimony is reduced.—Resembles the preceding compound in its physical properties and chemical relations; but its aqueous solution does not deposit pentasulphide of antimony, but only the tersulphide that may happen still to be mixed with it.

Hydrated Sulphantimoniate of Potassium or *Hydrosulphate of Antimonic Acid and Potash.*—1. Prepared by boiling a mixture of 11 parts of purified grey sulphide of antimony with 6 parts of carbonate of potash, 1 part of flowers of sulphur, 3 parts of burnt but afterwards slaked lime, and 20 parts of water, for two hours,—or by leaving the mixture at ordinary temperatures in a covered vessel for 24 hours, stirring frequently, then filtering, washing the residue, evaporating the filtrate, and, lastly, setting it aside to cool. (Liebig, *Handwörterb.* 1, 434.)—2. By fusing a mixture of bisulphate of potash, grey sulphide of antimony and charcoal, as in the preparation of the pure pentasulphide, (p. 355, β) then boiling the powdered mass with water and sulphur, and evaporating the filtrate to a thin syrupy consistence. (Geiger, *Mag. Pharm.* 29, 236.)—3. By fusing a mixture of monosulphate of potash, grey sulphide of antimony, charcoal, and sulphur, dissolving the resulting mass in water, and filtering the liquid. The product thus obtained is less than by method (1). (Rammelsberg.)—4. By boiling sulphantimonite of potassium with water and sulphur. The solution when sufficiently evaporated, yields, on standing, colourless granular, deliquescent crystals; but if the evaporation be carried too far, a radiated mass is obtained. (Geiger.) The crystals are yellowish, and fuse when heated, giving off water and leaving a brown mass. They deliquesce rapidly in the air, and become covered with kermes. (Rammelsberg.)

	Crystallized.		Rammelsberg.
3KS	165·6	36·35	36·679
SbS^5	209·0	45·87	45·167
9HO	81·0	17·78	18·154
$3KS,SbS^5+9Aq.$	455·6	100·00	100·000

When pentasulphide of antimony is dissolved in moderately strong solution of potash, and after dilution with water, precipitated by carbonate of ammonia or bicarbonate of potash, a kermes-coloured precipitate is formed, which, after prolonged washing and drying at 100°, contains potassium 3·06, antimony 55·40, and sulphur 39·45 (loss 2·09) per cent. (Rammelsberg.) This nearly corresponds to $KS,6SbS^5$, but the analysis gives rather too much sulphur.

G. **Compound of Sulphantimoniate of Potassium with Antimoniate of Potash.**—Pentasulphide of antimony dissolves in moderately concentrated solution of potash, with separation of a heavy white powder, consisting of bi-antimoniate of potash; the filtrate yields, on evaporation, long colourless needles, which, when exposed to the air, do not deliquesce, but acquire a brown coating. This salt is likewise produced by boiling tersulphide of antimony with sulphur, carbonate of potash, lime, and water. At a temperature a little above 100°, the salt loses its water of crystallization, turns yellow, and fuses to a reddish-brown mass, which becomes orange-yellow when cold. Acids precipitate from it a mixture of pentasulphide of antimony and antimonic acid or bi-antimoniate of potash, a small quantity of hydrosulphuric acid gas being at the same time evolved. Cold water dissolves it but partially, leaving a white powder of mono-antimoniate of potash; boiling water, on the contrary, dissolves it completely. If the antimonic acid be separated from the latter solution by chloride of barium, the filtrate evolves hydrosulphuric acid gas on the addition of acids, and gives a precipitate of pure pentasulphide of antimony. (Rammelsberg.)

	Crystallized.		Rammelsberg.
4K	156·8	23·03	22·60
2Sb	258·0	37·90	37·80
8S	128·0	18·80	18·20
6O	48·0	7·05	
10HO	90·0	13·22	13·30
$3KS, SbS^5 + KO, SbO^5 + 10Aq.$	680·8	100·00	

Or:

3KS	165·6	24·32
SbS^5	209·0	30·70
KO	47·2	6·93
SbO^5	169·0	24·83
10HO	90·0	13·22
	680·8	100·00

H. **Chloride of Antimony and Potassium.**—*a. With 2 Atoms of Chloride of Potassium.*—The aqueous solution of a mixture of 2 atoms of chloride of potassium and 1 atom of terchloride of antimony, yields oblique rhombic prisms. (Jacquelain, *Ann. Chim. Phys.* 66, 128.)

	Calculation.		Jacquelain	Or:		
2K	78·4	20·39	20·2	2KCl	149·2	38·81
Sb	129·0	33·56	32·8	$SbCl^3$	235·2	61·19
5Cl	177·0	46·05	46·3			
$2KCl, SbCl^3$	384·4	100·00	99·3		384·4	100·00

¶ *b. With 3 Atoms of Chloride of Potassium.*—$3KCl + SbCl^3$.—Crystallizes in laminæ. Deliquescent; decomposed by boiling water. (Poggiale, *Compt. rend.* 20, 1180.) ¶

ANTIMONY AND SODIUM.

A. ANTIMONIDE OF SODIUM.—*a.* Four parts of powdered antimony combine with one part of sodium at a temperature just above the melting point of antimony, the act of combination being attended with incandescence — Very brittle alloy, resembling bell-metal in its fracture, rapidly decomposed in the air, and effervescing strongly with water and aqueous acids. (Gay-Lussac & Thénard.)

b. When antimony is strongly ignited with an equal weight of tartrate of soda in a covered crucible for some hours, the result is a greyish black mass, which takes fire in the air and is decomposed by water. A mixture of antimony and soap, or of 8 parts of antimony with 4 parts of carbonate of soda and 1 part of charcoal, likewise yields a similar alloy. (Serullas.)

B. COMPOUND OF ANTIMONIC OXIDE AND SODA.—When 1 atom of antimonic oxide is fused with excess of carbonate of soda, 1 atom of carbonic acid is expelled: consequently the resulting compound is NaO,SbO^3. (Mitscherlich.) The greater part of the soda is extracted by water. (Mitscherlich, H. Rose.) A solution of antimonic oxide in solution of soda, after exposure to the air for some time, deposits crystals of antimoniate [antimonite?] of soda. (Mitscherlich.)

C. ANTIMONITE OF SODA.—Soluble in water. (Berzelius.)

D. ANTIMONIATE OF SODA.—¶ *a. Monohydrate.*—Fremy's *Acid Meta-antimoniate.*—NaO,HO,SbO^5.—Obtained by heating the salt *b* to between 180° and 200°. ¶—*b. With 7 atoms of water.*—When an aqueous solution of antimoniate of soda is supersaturated with caustic soda, this salt often separates in short, tabular, perpendicularly truncated square prisms. If the liquid also contains the compound of antimonic oxide and soda, that compound remains dissolved. (Mitscherlich.)—*b.* Antimoniate of soda is nearly insoluble in water. Hence a solution of antimoniate of potash added to a soda-salt gives, after some time, a crystalline antimoniate of soda free from potash. The solution of 1 part of a soda-salt in 350 parts of water is still precipitated in this manner, and even when the solution contains 100 parts of carbonate of potash to 1 part of carbonate of soda; but in a larger excess of carbonate of potash, the antimoniate of soda is slightly soluble. (Fremy, *Compt. rend.* 16, 187; also *N. J. Pharm.* 3, 97; also *J. pr. Chem.* 29, 86.) Antimoniate of soda is but very sparingly soluble in boiling water, and separates from the solution, on cooling, in brilliant, colourless, and transparent crystalline grains. (Gmelin.)

¶ According to Fremy, salts of soda are precipitated slowly, and frequently in rather large crystals, by the gummy pentahydrated antimoniate of potash, and immediately by the acid meta-antimoniate. In the former case, however, the antimoniate of soda is always more or less mixed with the flocculent precipitate which the insoluble antimoniate of potash gives with soluble salts. In testing for soda in organic salts, it is necessary first to convert them into carbonates, chlorides, or sulphates, —because antimoniate of potash often gives a flocculent precipitate with organic salts of potash after standing. The addition of alcohol renders the precipitation of the antimoniate of soda complete, but it is necessary to wash afterwards with water, to remove the other salts which are thrown down at the same time.

	Calculation.		Fremy.
NaO	31·2	11·86	12·0
SbO^3	169·0	64·21	64·3
7HO	63·0	23·93	24·0
$NaO,SbO^5 + 7Aq.$	263·2	100·00	100·3 ¶

Before the blowpipe, either of the three oxides of antimony gives with *carbonate of soda,* a glass which is transparent and colourless while hot, but white and opaque when cold. (Berzelius.)

E. *Borax* dissolves a large quantity of antimonious acid before the blowpipe, forming a glass which is transparent and yellow while hot, but which, if it contains a large excess of antimonious acid, becomes grey in the inner flame, from reduction of antimony. (Berzelius.)

F. *Microcosmic salt* likewise dissolves antimonious acid, producing a clear colourless glass, which in the outer flame appears yellowish when hot, and turns red if ferric oxide be present. (Berzelius.)

G. SULPHANTIMONITE OF SODIUM.—Also a *Liver of Antimony.*—*a.* A mixture of 177 parts (1 At.) of grey sulphide of antimony with 355 parts (9 At.) of monosulphide of sodium and between 15 and 17 parts of metallic antimony yields, by fusion at a gentle heat, a liver-coloured mass. (Kohl.)—*b.* A mixture of 15 parts of sulphide of antimony with 10 parts of fused Glauber's salt, exposed to a white heat in a covered charcoal crucible, yields, besides 0·5 metallic antimony, only 17 parts (because a portion of the compound volatilizes) of a reddish-brown dense mass, destitute of metallic lustre, but having a brilliant fracture. This substance deliquesces in the air, and is resolved by boiling water into insoluble kermes and a brown solution. (Berthier.)

Solution of Sulphantimonite of Sodium or *Hydrosulphate of Antimonic Oxide and Soda.*—177 parts of precipitated tersulphide of antimony require for solution 355 parts of aqueous sulphide of sodium. The solution is prepared by boiling; but with these proportions, no sulphide of antimony separates on cooling. (Kohl.) The solution gives a brownish-red precipitate with monocarbonate of potash or soda. (H. Rose.) A solution of tersulphide of antimony in boiling carbonate of soda deposits, after long exposure to the air, crystals of antimoniate of soda contaminated with kermes. (Mitscherlich.)

The crystals which are deposited from solutions of this kind, appear to consist of hydrated sulphantimoniate of sodium (Schlippe's salt), and not of hydrated sulphantimonite of sodium. Pagenstecher (*Repert.* 14, 112) ignited a mixture of 2 parts of grey sulphide of antimony with 4 parts of dry sulphate of soda and 1 part of charcoal; dissolved the resulting mass in 15 parts of boiling water; and obtained crystals by cooling or on the addition of alcohol. These colourless and transparent crystals, however, did not yield any kermes on the addition of acids, but only the golden sulphide; and their aqueous solution could not be made to take up an additional quantity of sulphur. Kohl (*N. Br. Arch.* 17, 263) dissolved the liver of antimony—obtained by fusing together at a gentle heat, 177 parts of tersulphide of antimony, 17 parts of metallic antimony, and

355 parts of protosulphide of sodium in the smallest possible quantity of boiling water, at the same time adding powdered antimony, and left the filtrate to crystallize on cooling. Or, again, he boiled a mixture of 177 parts of tersulphide of antimony, prepared in the wet way, with 355 parts of protosulphide of sodium, water, and a small quantity of powdered antimony. By these means he obtained pale yellow, regular tetrahedrons, containing 20·9 per cent. of protosulphide of sodium, 44·4 of tersulphide of antimony, and 34·7 of water. These crystals, when heated, lost water and left a yellowish-brown residue. They dissolved in hot concentrated hydrochloric acid, with the exception of a trace of sulphur. Their aqueous solution took up a large quantity of kermes at the boiling point, and again deposited it on cooling. When exposed to the air, it deposited kermes spontaneously; with acids, including the carbonic, and with alkaline bicarbonates, it immediately gave a precipitate of sulphide of antimony; and with monocarbonate of potash or soda, after some time, a precipitate having the colour of kermes, &c. Kohl himself, however, suspected that this salt contained a portion of Schlippe's salt mixed with it: according to Kircher's experiments, (*Ann. Pharm.* 31, 341) it consists almost entirely of that salt. Kircher obtained these tetrahedrons by boiling 2 parts of hydrated octohedral protosulphide of sodium (III., 96) with a small quantity of powdered antimony out of contact of air, and afterwards with 1 part of tersulphide of antimony, prepared in the wet way, till the whole was dissolved (whereby metallic antimony was separated, the quantity increasing considerably on cooling), and lastly covering the filtrate with a stratum of alcohol. The resulting crystals contained 23·60 per cent. of protosulphide of sodium, 41·50 of sulphide of antimony, and 35·18 of water; the sulphide of antimony, however, on being ignited in hydrogen gas, yielded metallic antimony corresponding in quantity to 25·5 per cent. in the crystals; whence it follows that the salt contained pentasulphide of antimony with a very small quantity only of the tersulphide. In other respects, the compound exhibited the properties mentioned by Kohl, and, like his salt, dissolved in hot concentrated hydrochloric acid, with separation of a small quantity of sulphur.

Another salt prepared by Kohl was probably more free from Schlippe's salt: the mode of preparation consisted in heating the mixture of 177 parts of sulphide of antimony and 354 parts of sulphide of sodium at a higher temperature—till in fact the fused mass became red hot—and then treating it, as above, with water, keeping it as much as possible from contact of air. The crystals thus obtained formed colourless and transparent prisms arranged in stellated groups, and contained 31 per cent. of sulphide of sodium, 25 of sulphide of antimony, and 41 of water. Moreover, they dissolved in hydrochloric acid with scarcely perceptible cloudiness, deliquesced in the air, and in other respects exhibited nearly the same properties as the tetrahedral salt.

H. SULPHANTIMONIATE OF SODIUM.—*Hydrated*—*Schlippe's Salt.*—1. Prepared by fusing 4 parts of grey sulphide of antimony with 8 parts of dry sulphate of soda and 2 parts of charcoal—boiling the mass, when cold, with water and 1 part of sulphur—and lastly filtering and setting aside to crystallize. Nine parts of crystals are hereby obtained; and the mother-liquid retains scarcely a trace of antimony, since it gives with acids a precipitate of nearly pure sulphur. (Schlippe, *Schw.* 33, 320.) During the fusion, a large quantity of metallic antimony separates, in consequence of the formation of pentasulphide of antimony; and the mother-liquid retains a considerable quantity of caustic soda: consequently, only the acid of part of the Glauber's salt is decomposed by the fusion, and the sulphur of that salt combines with the tersulphide of antimony, while the soda is set free; the latter is then converted, by boiling with sulphur, into pentasulphide of sodium and hyposulphite of soda, and does not further contribute to the formation of Schlippe's salt. If sulphur is added to the other ingredients, it volatilizes so quickly during the fusion that it does not assist in the formation of the compound. (Duflos, *Br. Arch.* 31, 94.)—2. A mixture of 24 parts of dry sulphate of soda with 4 parts of charcoal powder is ignited till the frothing ceases; the mass, after being poured out and cooled, is then boiled for half an hour with 6 times its weight of water, 18 parts of grey sulphide of antimony, and 3 parts of sulphur, and the liquid filtered and left to crystallize. 36 parts of crystals are thus obtained. By similarly treating a mixture of 8 parts of sulphate of soda, 2½ parts of charcoal, 1 part of sulphur, and 6 parts of sulphide of antimony, 12 parts of crystals are produced. The mother-liquid contains hyposulphite of soda. (Duflos.)—3. An intimate mixture of 24 parts of grey sulphide of antimony, 24 parts of dry carbonate of soda, 14 parts of sulphur, and 3 parts of charcoal, is ignited in a covered crucible—the resulting mass, when cold, dissolved in water—and the solution filtered. (*Pharmac. Boruss.*) The greater part of the sulphur volatilizes before fusion commences; consequently, 8 parts of metallic antimony are separated. On treating the mass with water, a large quantity of crocus antimonii remains undissolved, and the product of crystals amounts to only 6 parts. (Duflos.) F. C. Bucholz (*Br. Arch.* 33, 1) obtained by this process 10 parts of crystals, and by boiling the solution with sulphur, 12 parts. The fusion should be continued till the mass no longer swells up much; for if it be sooner stopped, carbonate and sulphate of soda—the latter produced at the commencement by the action of sulphur on the carbonate of soda—remain undecomposed; and if the fusion be prolonged till the mass ceases altogether to evolve carbonic oxide, it gives off sulphur and becomes oxidized, and when subsequently dissolved in water, yields a large quantity of kermes and fewer crystals. (Jahn, *N. Br. Arch.* 22, 43.)—4. A mixture of 72 parts of elutriated grey sulphide of antimony, 13 parts of flowers of sulphur, 48 parts of dry carbonate of soda, and 52 parts of burnt lime, is boiled with water in an iron vessel for 2 or 3 hours, then filtered, and evaporated to the crystallizing point. (Mitscherlich.) Or a mixture of 9 parts of sulphide of antimony, 3 parts of flowers of sulphur, 18 parts of crystallized carbonate of soda, 5 parts of lime previously slaked with 5 parts of water, and 80 parts of water, is treated precisely in the same manner. By decanting the mother-liquid from the crystals, and boiling a second time with the residue, a further crop of crystals is obtained. The total quantity of crystals amounts to 15 parts. (Frederking, *N. Br. Arch.* 28, 64.) Or again, a mixture of 11 parts of sulphide of antimony, 1 part of flowers of sulphur, 13 parts of crystallized carbonate of soda, and 5 parts of burnt lime previously slaked with 20 parts of water may be used. The same ingredients may likewise be left in a closed vessel for 24 hours at ordinary temperatures, the whole being frequently shaken. (Liebig, *Handwörterb.* 1, 433.)—5. A solution of soda liver of sulphur is saturated with sulphide of antimony and sulphur at a boiling heat, and the liquid filtered. (Liebig.) The salt likewise crystallizes from a solution of pentasulphide of antimony in caustic soda, and from liquid soap of antimony. (Schlippe.) A small quantity of caustic soda must be added during the evaporation, to prevent the precipitation of kermes, whereby the crystals would be rendered impure. (Pfaff.)

¶ 6. Janssen (*J. pr. Chem.* 33, 336) projects an intimate mixture of 4 parts (3 At.) of crystallized sulphate of soda, 3½ parts (1 At.) of tersulphide of antimony, and 1 part of charcoal into a red-hot crucible, and ignites the mixture out of contact of air till it fuses tranquilly; he then adds $\frac{5}{8}$ pt. (2 At.) of sulphur, stirs well, and pours the whole out. The fusion must not be continued too long, otherwise the tersulphide of antimony will be converted into antimonic oxide, and then reduced by the charcoal. The liver of antimony thus obtained is exhausted with water (to which, when crude sulphide of antimony has been used, a small quantity of caustic soda is added to precipitate oxide of iron), and the filtrate evaporated to the crystallizing point. It may likewise, according to Janssen, be obtained in the wet way, by gradually adding tersulphide of antimony to a boiling solution of pentasulphide of sodium, and then mixing the liquid with caustic soda, till the sulphur, which at first separates in large quantity, is nearly redissolved—then again adding tersulphide of antimony—and so on. The pentasulphide of sodium should remain in excess, which may easily be known by dropping the liquid into solution of hydrosulphuric acid, when a white cloud is formed if any of the salt is still present. The solution is lastly filtered and evaporated, whereupon crystals of the pure salt are deposited.

7. A mixture of 8 parts of effloresced sulphate of soda, 6 parts of sulphide of antimony, and 3 parts of charcoal, is projected into a red-hot hessian crucible; the cover put on; the mixture heated till it ceases to froth up, and then boiled with 1 part of sulphur and a sufficient quantity of water. The solution, soon after cooling, deposits colourless or pale yellow tetrahedrons, which are insoluble in alcohol, but dissolve in 3 parts of cold water. (Van den Corput, *Chem. Gazette*, 1848, 268.) ¶

The crystals, obtained by either of these processes, are washed with a small quantity of cold water; dried, first between blotting-paper and then under a receiver beside oil of vitriol; and lastly preserved in well-stopped bottles.

Pale yellow, almost colourless, transparent regular tetrahedrons, having either the terminal edges replaced by planes (*Fig.* 14), or acuminated with 3 faces (those of the rhombic-dodecahedron) resting on the faces of the tetrahedron. Sometimes also the edges of the tetrahedron are replaced by six-sided summits, corresponding to those of the pyramidal cube. (*Fig.* 9.) (Rammelsberg.) The crystals have a bitter alkaline and metallic taste. When pure, they remain colourless in the air, and if kept dry, undergo very little change; but when they contain the compound of antimonic oxide and soda, they rapidly change colour in the air. (Janssen.)

	Crystallized.		Rammelsberg.	Schlippe.	Duflos.
3NaS	117·6	24·07	24·36	24·17	21·76
SbS^5	209·0	42·77	42·29	41·72	56·75
18HO	162·0	33·16	33·35	34·03	20·50
$3NaS, SbS^5 + 18Aq$	488·6	100·00	100·00	99·92	99·01

The crystallized salt loses 20·5 per cent. of water when pulverized and dried in vacuo over oil of vitriol. (Duflos.) When heated out of contact of air, it melts in its own water of crystallization, after the expulsion of which there remains a greyish-white mass; this, when exposed to the air, crumbles to a bulky powder; or if strongly heated out of contact of air, fuses to a liver-coloured mass, which, on being dissolved in water, leaves but a small residue of sulphide of antimony. (Rammelsberg.) When ignited in a current of hydrogen gas, it gives off its water of crystallization, but no sulphur. (H. Rose.) When heated on the open fire, it effloresces, rapidly turns red, and then black, burning with a sulphurous flame and leaving a white mass. (Schlippe.) When a concentrated solution of the salt is exposed to the air, it deposits pentasulphide of antimony in the form of a granular powder; and hyposulphite of soda is formed in it; a dilute solution on the contrary, deposits white crystalline flakes of bi-antimoniate of soda. (Liebig, *Ann. Pharm.* 7, 13.) This decomposition is effected by the carbonic acid in the air; for when air freed from carbonic acid is passed through the [concentrated?] solution, no change is produced. A solution which has been perfectly decomposed by many months' exposure to the air, contains carbonate and hyposulphite (no sulphate) of soda; and the dark reddish brown precipitate, which colours the wash-water yellow and becomes lighter, contains, after washing, 1·94 per cent. of sodium, 66·39 of antimony, and 30·11 of sulphur (loss 1·56). This percentage gives $1Na, 6Sb, 23S = NaS, 2SbS^5, 4SbS^3$; hence the pentasulphide must lose a portion of its sulphur, which then serves for the formation of the hyposulphite of soda. (Rammelsberg.) The fact of the imperfectly dried crystals becoming brown in the air likewise depends on this decomposition. All acids, including even carbonic acid, decompose the solution, precipitating pentasulphide of antimony and liberating hydrosulphuric acid:

$$3NaS, SbS^5 + 3SO^3 + 3HO = 3(NaO, SO^3) + SbS^5 + 3HS.$$

By boiling with excess of hydrochloric acid, the pentasulphide of antimony is dissolved, with separation of sulphur. Carbonic acid gas passed through the solution, precipitates only the greater part of the pentasulphide; but if the filtrate, which is only slightly clouded by carbonic acid gas, be freed by boiling from the hydrosulphuric acid accumulated in it, the remainder of the pentasulphide of antimony is precipitated on treating it with a fresh current of carbonic acid gas. (Gmelin.) Alkaline monocarbonates do not throw down a brownish-red precipitate from the solution of this salt, as they do from a solution of sulphantimonite of sodium. (H. Rose.) On mixing a solution of tartar-emetic with a solution of Schlippe's salt, an orange-coloured precipitate is produced. This precipitate contains $2Sb, 4S, 3O$, which may be reduced to the formula: SbO^3, SbS^4 or $2SbO^3, SbS^3, SbS^5$. Of the 3 atoms of SbO^3 contained in 3 atoms of tartar-emetic, 2 atoms remain undecomposed; the third SbO^3 reacts upon $3NaS$, forming SbS^3 and $3NaO$. (Rammelsberg.) By boiling a solution of the salt with sulphur for several hours, it is entirely decomposed, a kermes-coloured powder being precipitated. (Gmelin.) The aqueous solution at its boiling point dissolves antimonic oxide, and on cooling deposits a grey compound, which contains 30·5 per cent. of antimonic oxide and 69·5 of kermes; when an excess of antimonic oxide is used, the above precipitate is accompanied by crystalline grains of the compound of antimonic oxide and soda. (Duflos.) By boiling the solution with powdered antimony, the sulphantimoniate of sodium is converted into sulphantimonite of sodium, which deposits a large quantity of kermes on cooling, still more on the addition of common salt, and the remaining portion on the addition of an acid (p. 348). (Duflos.) The solution dissolves grey sulphide of antimony when boiled with it, and, on cooling, deposits it again in the form of kermes without further decomposition. (Duflos.) The boiling solution does not take up pentasulphide of antimony. (Rammelsberg.) The salt dissolves in 2·9 parts of water at 15° (Rammelsberg), in 4 parts of cold, and in 1 part of boiling water. (Duflos.) It is not soluble in alcohol, even when the alcohol is rather largely diluted with water. (Rammelsberg.)

I. Chloride of Antimony and Sodium.—Terchloride of antimony dissolves in solution of common salt without producing a precipitate, and the solution yields large crystals on evaporation. (Liebig, *Handwörterb.* 1, 423.) Crystallizes in plates, having the composition $3NaCl,SbCl^3$. (Poggiale.)

Antimony and Barium.

A. Antimonite of Baryta.—When a boiling dilute solution of antimonite of potash is added slowly and in small quantities at a time to a boiling dilute solution of chloride of barium, small flat needles, having a silvery lustre, are deposited. These crystals are permanent in the air, difficultly soluble in water, and give up baryta to acids. (Berzelius.)

B. Antimoniate of Baryta.—White powder; not decomposible by carbonic acid; scarcely soluble in water. (Berzelius.)

C. Sulphantimonite of Barium.—1. Prepared by strongly igniting a mixture of sulphide of antimony with heavy spar and charcoal.—Reddish-brown, slag-like, infusible mass, which dissolves in water, with separation of a yellowish-brown powder. (Pagenstecher.)—The transparent tables and radiated crystals, which Pagenstecher obtained by evaporating and cooling a solution of this salt, and which, when exposed to the air, rapidly turned yellow and then red,—or when dissolved in water, evolved hydrosulphuric acid gas, and gave a yellowish-red precipitate—probably belong to the next compound.

D. Sulphantimoniate of Barium.—*Hydrated.*—Obtained by dissolving pentasulphide of antimony in solution of sulphide of barium, evaporating the yellowish filtrate to a small bulk, and then mixing it with alcohol.—Unless alcohol is added, the crystallization is difficult. When pentasulphide of antimony is dissolved in baryta-water, antimoniate of baryta is separated, and the same compound formed.—By igniting a mixture of heavy spar with charcoal, grey sulphide of antimony, and sulphur, and exhausting the mass with water, a few crystals are also obtained.—White needles, arranged in stellate masses. When exposed to the air, they turn brown, from separation of pentasulphide of antimony. When heated, they leave a brown mass without previously fusing. (Rammelsberg.)

	Calculation.		Rammelsberg.
3BaS	253·8	49·11	48·85
SbS^5	209·0	40·44	41·18
6HO	54·0	10·45	9·91
$3BaS,SbS^5+6Aq.$	516·8	100·00	99·94

¶ E. Chloride of Antimony and Barium.—$2BaCl,SbC+5Aq.$—Formed by adding a strong solution of chloride of barium to acid hydrochlorate of antimonic oxide. Crystallizes in fine needles grouped in stellate masses. Similar compounds may likewise be obtained with strontia, lime, and magnesia. (Poggialo.) ¶

ANTIMONY AND STRONTIUM.

SULPHANTIMONIATE OF STRONTIUM.—*Hydrated.*—When an aqueous solution of sulphide of strontium is saturated with pentasulphide of antimony, a solution is formed which does not crystallize, but, on the addition of alcohol, deposits this compound in the form of a dense, oily liquid. The liquid contains rather more than 3 atoms of SrS to 1 atom of SbS^5. (Rammelsberg.)

ANTIMONY AND CALCIUM.

A. ANTIMONITE OF LIME.—Prepared by double decomposition.—White crystalline powder, insoluble in water. (Berzelius.)

B. ANTIMONIATE OF LIME.—Obtained likewise by double decomposition.—White semi-crystalline powder, nearly insoluble in water. (Berzelius.)

Romeite.—Square octohedrons (*Fig.* 21) $e : e'' = 111°$; $e : e$ behind $= 69°$. (Dufrénoy.) Insoluble in acids before ignition with carbonate of potash; contains in 100 parts: lime 16·67, manganous oxide 2·60, ferrous oxide 1·20, antimonious acid (or perhaps one of the other oxygen compounds of antimony) 79·31, silica 0·64 (excess 0·42). (Damour.) Hence the formula is about (CaO; MnO; FeO), SbO^4; though the quantity of SbO^4 is rather too small.

C. SULPHANTIMONIATE OF CALCIUM.—The product obtained by igniting out of contact of air a mixture of grey sulphide of antimony, sulphur, and caustic lime or its carbonate, is the *Calx Antimonii cum Sulphure Hoffmanni.* The following are the proportions recommended: 4 pts. of sulphide of antimony, 3 pts. of sulphur, and 10 pts. of burnt oyster shells. (Bremser.)—1 pt. of sulphide of antimony, 2 pts. of sulphur, and 8 pts. of purified oyster shells (*Pharmacopœia Boruss. ed. 5.*)—1 pt. of sulphide of antimony, 1 pt. of sulphur, and 4 pts. of purified chalk. (Bucholz.)—The result is a mixture, either of sulphantimoniate of calcium and a compound of antimonic oxide with lime, or of sulphantimoniate of calcium and sulphate of lime.—If the ignition be stopped too soon, a brown powder is obtained; but by continuing it for upwards of an hour, a brownish-yellow or yellowish-white powder is produced, which must be preserved in well-closed bottles, as it evolves hydrosulphuric acid in the air, and turns brown. When repeatedly boiled with a large quantity of water, it dissolves partially—the solution (*Solutio Calcis Antimonii cum Sulphure*) evolving sulphuretted hydrogen on the addition of hydrochloric acid, and depositing pentasulphide of antimony, which, when the mixture has been sufficiently ignited, amounts to about $\frac{2}{3}$ of the sulphide of antimony originally used.

By boiling 1 part of grey sulphide of antimony with water and 3 parts of lime, a colourless filtrate is obtained, which has a hepatic taste, and, when evaporated in a retort to a small bulk, deposits a yellowish-white, amorphous powder, which turns brownish-red in the air, and gives a precipitate of pentasulphide of antimony with acids, and of pentasulphide of antimony and lime with alcohol,—so that the filtrate no longer evolves hydrosulphuric acid on the addition of acids. (Pagenstecher, *Repert.* 14, 217.)

By boiling pentasulphide of antimony with sulphide of calcium and water, a yellow solution is obtained, which does not yield any crystals, but deposits an oily liquid on being mixed with alcohol. The solution contains 33·7 per cent. of pentasulphide of antimony and 66·3 of protosulphide of calcium. (Rammelsberg.) [This must be an error of the press in Rammelsberg's memoir; for since, according to Rammelsberg, the compound consists of $3CaS,SbS^5$, the 66·3 must belong to the sulphide of antimony, and the 33·7 to the sulphide of calcium.]

ANTIMONY AND MAGNESIUM.

SULPHANTIMONIATE OF MAGNESIUM.—By dissolving pentasulphide of antimony in water wherein hydrate of magnesia is diffused and through which a current of hydrosulphuric acid is passed, a yellow uncrystallizable liquid is obtained, from which alcohol precipitates an orange-coloured substance, composed of $3MgS,SbS^5$, nearly. (Rammelsberg.)

ANTIMONY AND SILICIUM.

HYDROFLUATE OF SILICA AND ANTIMONIC OXIDE.—Crystallizes by slow evaporation, in prisms which crumble to powder when dried in the air, and dissolve readily in water if an excess of acid is present. (Berzelius.)—A mixture of sulphide of antimony and antimonic oxide imparts a yellow or hyacinth-red colour to glass.

ANTIMONY AND MOLYBDENUM.

MOLYBDATE OF ANTIMONIC OXIDE.—Precipitated as a yellow powder, which is soluble in boiling water. (Berzelius.)

ANTIMONY AND VANADIUM.

VANADIATE OF ANTIMONIC OXIDE.—A solution of tartar-emetic gives with vanadiate of ammonia a yellowish red-brown coagulum, which dissolves in the liquid on agitation, forming a solution of the same colour. (Prideaux.)

ANTIMONY AND CHROMIUM.

CHROMATE OF ANTIMONIC OXIDE.—Chromate of potash gives with acid hydrochlorate of antimonic oxide, a brownish-yellow precipitate, which dissolves in an excess of the antimony-salt, forming a green solution (Thomson): probably from formation of chromic oxide.

ANTIMONY AND URANIUM.

A. ANTIMONIATE OF URANOUS OXIDE.—Hydrochlorate of uranous oxide gives with an excess of mono-antimoniate of potash, a gelatinous green precipitate, easily soluble in excess of the hydrochlorate of uranous oxide. The precipitate when ignited loses 14·75 per cent. of water, and turns yellowish-brown. Boiling solution of potash extracts the whole of the antimonic acid from the precipitate while still moist, but only a portion after drying. Nitric acid separates the uranium in the form of uranic oxide, leaving the antimonic acid unaltered. Hydrochloric acid dissolves the salt only when hot and in a concentrated state; the solution deposits antimonic acid on the addition of water. (Rammelsberg, *Pogg.* 59, 27.)

	Approximate calculation.		Rammelsberg.
5UO	340	34·62	34·94
$3SbO^5$	507	51·63	
15HO	135	13·75	14·75
$5UO, 3SbO^5 + 15Aq$	982	100·00	

B. URANIC SULPHANTIMONIATE.—A compound of pentasulphide of antimony with sesquisulphide of uranium.—A solution of sulphantimoniate of sodium gives a yellowish-brown precipitate with hydrochlorate of uranic oxide and ammonia. (Rammelsberg.)

ANTIMONY AND MANGANESE.

A. ANTIMONIATE OF MANGANOUS OXIDE.—Prepared by double decomposition.—Snow-white, permanent in the air, sparingly soluble in water. When ignited, it turns grey, but at a higher temperature, again becomes white, without exhibiting any glow; after this, acids have no longer the power of separating the manganous oxide.—(Berzelius.)

B. SULPHANTIMONIATE OF MANGANESE.—The solution of sulphantimoniate of sodium gives with sulphate of manganous oxide, a white cloudiness, and after a while, a dense reddish-brown precipitate, which is not altered by boiling with the supernatant liquid, but becomes reddish-grey when washed and dried, in consequence of oxidation. (Rammelsberg.)

ANTIMONY AND ARSENIC.

A. ARSENIDE OF ANTIMONY.—*a.* Seven parts of antimony unite with one part of arsenic, forming a grey, hard, very brittle and fusible mass. (Bergman.)—*b.* By heating a mixture of 15 parts of powdered antimony and 20 parts of powdered arsenic, 16·1 parts of arsenide of antimony are formed, without any emission of light or heat. This alloy is as brittle and has the same laminar structure as antimony, but is whiter, and fuses readily. (Gehlen.) By exposure to a white heat, out of contact of air, the arsenic is completely volatilized; also in a current of hydrogen gas, even at a low red heat. (Liebig.)—*c.* Found native, having a fine granular fracture, and specific gravity = 6·13 (Thomson), 6·203 (Rammelsberg.) Gives up all its arsenic when ignited in a current of hydrogen gas. (Rammelsberg.)

	Native.		Rammelsberg.	Thomson.
Sb	129	36·44	37·85	46·61
3As	225	63·56	62·15	38·51
$SbAs^3$	354	100·00	100·00	85·12

B. Arsenite of Antimonic Oxide.—When an aqueous solution of arsenic acid is digested with antimony, arsenite of antimonic oxide is formed, and is precipitated on diluting with water. (Berzelius.) This salt may also be obtained in the dry way, by heating arsenic with antimonic acid; it then forms a transparent, vitreous, fused mass.

C. Arseniate of Antimonic Oxide.—Arseniate of potash produces a white pulverulent precipitate in acid hydrochlorate of antimonic oxide. (Berzelius.)

D. Arseniate of Antimonic Acid.—Formed by heating a substance which contains both arsenic and antimony, with nitric acid, and diluting the solution with water; whereupon the compound is precipitated as a white powder, soluble in nitric or hydrochloric acid. The latter solution, when evaporated to a small bulk and treated with water, is resolved into antimonic acid which is precipitated, and arsenic acid which dissolves; the latter may be purified from the still adhering antimonic acid by repeated evaporation to dryness and re-solution in water. (Berthier.)

E. Compound of Tersulphide of Arsenic with Tersulphide of Antimony.—Aurora-red precipitate, which fuses readily to an orange-yellow, transparent liquid. (Berzelius.)

F. Compound of Pentasulphide of Arsenic with Tersulphide of Antimony.—The sodium compound precipitates from salts of antimonic oxide a reddish-yellow, easily fusible substance. (Berzelius.)

G. Arsenide of Antimony and Potassium.—Prepared by igniting a mixture of 2 parts of antimony with 1 part of arsenious acid and 2 parts of cream of tartar in a covered crucible, for two hours. The alloy evolves arseniuretted-hydrogen gas with water. (Serullas.)

Other Compounds of Antimony.

With Bismuth, Zinc, Tin, Lead, Iron, Cobalt, Nickel, Copper, Mercury, Silver, Gold, Platinum, and Palladium. These alloys are brittle and white when the antimony predominates.

CHAPTER XXVI.

TELLURIUM.

Müller v. Reichenstein. *Abhandl. einer Privatgesellschaft in Böhmen. Jahrg.* 1, *Quart.* 1, 2, and 3.
Klaproth. *Crell. Ann.* 1798, 1, 91; also his *Beiträge*, 3, 1.—Further, *Gilb.* 12, 246.
Sir H. Davy. Hydrotelluric acid. *Phil. Trans.* 1810, 27; also *Schw.* 5, 348; also *Gilb.* 37, 48.
Berzelius. *Schw.* 6, 311; 34, 78.—Sulphotellurates. *Pogg.* 8, 411.—Tellurium in general. *Pogg.* 28, 392; 32, 1 and 577.

SYNONYMES. *Sylvan, Tellur, Tellure.*

History. Müller v. Reichenstein, in 1782, showed that tellurium ores contain a peculiar metal—a statement which was confirmed by Klaproth, in 1798. Hydrotelluric acid was discovered by Sir Humphry Davy. For nearly all the other facts relating to tellurium, we are indebted to the untiring labours of Berzelius.

Sources. As native tellurium (containing small quantities of iron and gold); as tellurous acid; as telluride of bismuth; as telluride of lead, associated likewise with foliated tellurium; as telluride of silver; as yellow tellurium and graphic tellurium (telluride of gold and silver).

Preparation. a. From *Telluric Bismuth*, which contains about 60 per cent. of bismuth, 36 tellurium, and 4 sulphur—sometimes also selenium, silver, and matrix.

The ore is pulverized; the earthy portions, which contain telluric oxide, and are therefore useful, are separated by washing; the metallic powder mixed with an equal weight of carbonate of potash or soda, and made up into a stiff paste with olive oil; the mixture heated in a well-closed porcelain crucible, carefully at first (to prevent frothing over) till the oil has become carbonized, and afterwards to a full white heat. The whole is then left to cool with the cover on; the dark brown porous mass quickly pulverized; the powder thrown on a filter; water exhausted of air by boiling and then cooled out of contact of air, is poured upon it; and lastly, it is washed thoroughly by means of the wash-bottle with water thus exhausted, the air being all the time excluded as completely as possible. The residue left on the filter consists of charcoal, bismuth, and a trace of tellurium. The tellurium is precipitated from the dark-red filtrate by blowing air through it with the bellows, and then collected on a filter. The filtered liquid thus obtained is yellow, and contains sulphide and selenide of tellurium, dissolved by sulphide of potassium; these compounds may be precipitated by hydrochloric acid. The tellurium, after being washed on the filter, is fused, and subsequently freed by distillation from gold, iron, copper, and manganese, which are left behind in combination with a small quantity of tellurium. As the distillation of tellurium requires a high temperature, the fused metal is placed in an elongated dish, and introduced into a slightly inclined porcelain tube, through which, during the ignition, a stream of hydrogen gas is passed. (Berzelius.)

The object of fusing with carbonate of potash and charcoal is to free the tellurium from sulphur, selenium, and arsenic. The arsenic volatilizes, and the sulphur, together with the selenium, remains dissolved, after the current of air has been passed through the aqueous solution, provided that solution contains excess of alkali. The three substances just mentioned cannot be separated from tellurium by simple distillation. (Berzelius.)

b. From *Telluride of Silver*, containing 35 per cent. of tellurium, from 61 to 46 of silver, and from 1 to 18 of gold.—1. Two bulbs are blown on a glass tube half an inch apart, and the telluride of silver is heated in one of them, while a current of chlorine gas is passed through the tube, the heat being kept up till the chloride of silver formed in the first bulb fuses to a transparent liquid, containing no insoluble residue. Protochloride of tellurium is first formed, and mixes with the chloride of silver, producing a black liquid; more chlorine is then absorbed and bichloride of tellurium formed, which distils over into the second bulb. When the chlorine which escapes is passed through water, it gives up chloride of sulphur, chloride of selenium, a trace of chloride of antimony, and a small quantity of chloride of tellurium. When the decomposition is completed, the tube is cut in two between the bulbs; the chloride of tellurium distilled over into the second bulb is dissolved in dilute hydrochloric acid, and the tellurium precipitated from the solution by bisulphite of potash. Hydrosulphuric acid added to the filtrate precipitates a trace of kermes. The tellurium obtained by this process is purified by distillation in a current of hydrogen, whereupon the greater part of the selenium mixed with it volatilizes in the form of a red vapour; nevertheless a trace of selenium remains mixed with the tellurium.—2. The telluride of silver is first broken up in a mortar, and rubbed to powder with water. One part of the powder is then mixed with 1 pt. nitre and 1⅓ pt. carbonate of potash, and the mixture heated in a silver crucible, not quite to redness, till the black colour changes to reddish-grey; the heat is then increased to redness, the mass left to cool, and then exhausted with water, which leaves the silver behind in a state of purity. The clear filtrate, which becomes milky when heated, is evaporated to a small bulk—then mixed with a large quantity of charcoal powder, and evaporated to dryness—the mass pressed into a crucible, which is then covered and heated to redness—and the separation of the tellurium completed as in the extraction of the metal from telluride of bismuth. (Berzelius.)—3. The finely pounded ore is heated in a retort having a receiver adapted to it, with tolerably strong nitric acid free from chlorine, till the whole is oxidized; the liquid is then distilled to dryness; the nitrate of silver extracted from the residue with water; the residual tellurous acid ignited with carbonate of potash and oil; and the extraction of the tellurium completed as from telluride of bismuth. The charcoal which remains after exhaustion with water, contains but a small quantity of reproduced telluride of silver. (Berzelius.)—

4. One part of pounded telluride of silver is introduced in successive portions into a crucible containing 1 part of carbonate of potash in a state of fusion; a stronger heat is afterwards applied, and the crucible broken when cold. A small quantity of silver is found at the bottom; above it is a layer of telluride of silver; and at the top, a stratum of carbonate of potash, which contains a small quantity of tellurous acid and is to be kept for the treatment immediately to be described. The telluride of silver thus obtained is pounded up and again added in successive portions to an equal weight of carbonate of potash, each portion of telluride of silver, however, being mixed with nitre. The effervescence produced on the addition of each portion of nitre and telluride of silver must be allowed to subside before a fresh quantity is added. After the whole has been added, the mass is left to cool, and the crucible broken. The whole of the silver is found at the bottom, in a state of perfect purity, and the whole of the tellurium above it in the form of tellurate of potash. This salt (together with the carbonate and tellurite of potash formerly obtained) is mixed with a small quantity of charcoal, and thrown by small portions at a time into a red-hot crucible, each portion being added as soon as the effervescence caused by the last has subsided: if the quantity of charcoal is insufficient, a piece of charcoal is placed upon the surface of the melted mass. This mass, which consists of telluride of potassium and carbonate of potash, is then, after cooling, dissolved in a tolerably large quantity of water, the carmine-coloured solution exposed to the air in flat dishes till it has lost its colour, and the precipitated tellurium collected on a double filter, and washed, first with water, then with a small quantity of hydrochloric acid, then again with water, and fused together after drying. (Hess. *Pogg.* 28. 407.)

c. From *Foliated Tellurium*, which contains 13 per cent. of tellurium, 63 lead, together with copper, gold, antimony, and sulphur—probably in the form of telluride of gold, sulphide of lead, and sulphide of antimony. —1. The finely pounded ore is freed from the metallic sulphides by repeated boiling with strong hydrochloric acid and washing with boiling water; the residual telluride of gold treated with nitric acid; the tellurium solution poured off from the gold and evaporated to dryness; the residue of telluric oxide dissolved in hydrochloric acid; and the tellurium precipitated from the solution by sulphurous acid. (Berthier.)—2. A mixture of 10 parts of the ore, 8 or 9 parts of nitre, and 20 parts of dry carbonate of potash or soda is heated to complete fusion in an earthen crucible; the mass poured out, pulverized, and mixed with 8 or 9 parts of nitre and 10 parts of fresh ore; the fusion repeated; and the melted mass poured out, pulverized, and again fused in the same crucible with 10 parts of fresh ore and 8 or 9 of nitre: at the third fusion, however, a stronger heat is applied, the fused mass left to cool in the crucible, the crucible broken, and the greyish-white, crystalline regulus, amounting to about 15 per cent., separated from the slag. The latter is pulverized, dissolved in a large quantity of water, and the solution filtered from the oxides of lead and antimony. (As these oxides often still contain gold, they are reduced with black flux, and the gold separated by cupellation.) The alkaline liquid is supersaturated with sulphuric or hydrochloric acid; separated from the precipitated gelatinous silica; the tellurium precipitated from it by the immersion of iron rods; and the black powder, after washing and drying, fused together in a glass tube or a retort. The tellurium thus separated is free from iron, provided the iron rods are perfectly bright and the liquid kept strongly acid. [Antimony may, however, be mixed with it.] The liquid filtered from the tellurium should no longer give a precipitate with hydrosulphuric acid. If the metallic regulus obtained as above be heated with nitric acid, which takes up lead and sometimes also a small quantity of tellurium—then with hydrochloric acid—and afterwards thoroughly washed, a residue of pure gold is obtained. (Berthier, *Ann. Chim. Phys.* 51, 156.)

d. From *Native Tellurium,* which contains 97 per cent. of tellurium, together with small quantities of iron, gold, and sulphur. It is dissolved in aqua-regia; the solution diluted with as much water as can be added without producing a precipitate, and then supersaturated with caustic potash; and the liquid, which contains tellurite of potash, filtered from the oxides of iron and gold, and neutralized exactly with hydrochloric acid. The precipitate of telluric oxide, after being washed and dried, is mixed with oil, or with $\frac{1}{10}$ of its weight of charcoal, and heated in a glass retort. The reduced tellurium partly collects at the bottom of the retort, and partly sublimes in the neck. (Klaproth.)—Since tellurous acid precipitated by Klaproth's method contains potash, the tellurium reduced from it contains potassium, which must be separated by fusion with a small portion of tellurous acid. (Berzelius.)

[Gersdorf and Kölreuter's modes of preparation. (*N. Tr.* 8, 2, 285; *Schw.* 62, 213.)—Separation of tellurium from selenium, according to Berzelius (*Pogg.* 32, 11), according to Wehrle. (*Zeitschr. Phys. Mat.* 3, 317.]

To purify telluric oxide from the oxides of lead, copper, &c. it must be dissolved in bihydrosulphate of potash; filtered from sulphide of lead, sulphide of copper, &c.; the sulphide of tellurium precipitated from the filtrate by acids, and heated in a retort at a very gradually increasing temperature, till the whole of the sulphur, together with any selenium and arsenic that may be present, has passed over. If the heat be raised too quickly, a small quantity of tellurium likewise volatilizes. (Berzelius.) [For the separation of tellurium by sulphurous acid, see page 399 [·

Properties.—Crystalline system the rhombohedral. Primary form, an acute rhombohedron, (*Fig.* 151); also (*Figs.* 153, 135,) a six-sided prism shortened to a table; also an obtuse rhombohedron. (*Fig.* 141); $r^3 : r^5$ (*Fig.* 141), according to Phillips=115° 12′; also $r^3 : r^5$ (*Fig.* 151) =86° 3′. Cleavage parallel to *r* and *p* (*Figs.* 151 and 153). Breithaupt, *Pogg.* 7, 527; *Schw.* 52, 168.) On distilling tellurium in hydrogen gas, (p. 394,) a portion of it sublimes in shining, flat, elastic needles. (Berzelius.) When tellurium solidifies quietly after fusion, its surface exhibits a crystalline structure. (Berzelius.) Specific gravity, 6·115 (Klaproth), 6·1379 (Magnus), 6·2445 (Berzelius), 6·343. (Reichenstein.) Very brittle; easily pulverized.—Tin-white, with strong metallic lustre. —When obtained in the finely divided state by precipitation or sublimation, it forms a brown powder. (Magnus.) When precipitated by the action of the air from a very dilute solution of hydrotellurate of potash, it causes the liquid to appear blue by transmitted light. (Berzelius.)—Fuses less easily than lead, rather more easily than antimony; after fusion, it contracts very strongly on cooling. Hence, when it is slowly cooled, a large cavity is formed in the middle of the mass; when, on the contrary, the cooling is rapid, the surface solidifies, while the interior still remains liquid; and as the inner part solidifies, numerous small cavities are formed in it, which diminish the specific gravity. (Berzelius.) Tellurium boils at a temperature higher than the softening point of glass, and is then converted into a yellow vapour, having the colour of chlorine gas. (Berzelius.) When heated to redness in a retort, it sublimes in the neck, in the form of shining drops. (Klaproth.)

Compounds of Tellurium.

TELLURIUM AND OXYGEN.

Berzelius did not succeed in forming a protoxide of tellurium. 64 parts Te and 80 parts TeO^2 intimately mixed and heated to various degrees did not form a definite compound. Protochloride of tellurium decomposed by dry carbonate of soda yielded a mixture of tellurium and tellurous acid, &c.

A. TELLURIC OXIDE OR TELLUROUS ACID. TeO^2.

Found native in small white beads having a tinge of greyish-yellow and a crystalline texture. (Petz, *Pogg.* 57, 477.)

Formation.—Tellurium heated in the air somewhat above its melting point, burns with a bright blue flame green at the edges, and is converted into a white cloud—which, according to Berzelius and Magnus, has a faint, unpleasant odour, different from that of selenium—and condenses on cold bodies in the form of a white oxide. The horse-radish odour, which Klaproth observed at the same time, proceeded from an admixture of selenium.—2. Nitric acid and heated sulphuric acid convert tellurium into telluric oxide, the former giving off nitric oxide, the latter sulphurous acid. Tellurium does not decompose vapour of water at a red heat. (Regnault.)

Preparation.—A solution of tellurium in nitric acid is left to itself for a considerable time: the purer and more concentrated it is, the more quickly does the telluric oxide separate from it in the crystalline form. The oxide thus deposited does not contain more than ½ per cent. of nitric acid, which, on the application of heat, is given off with some decrepitation. (Berzelius.)—2. A solution of tellurium in nitric acid is evaporated to dryness and gently ignited. (Berzelius.)—3. A boiling solution of bichloride of tellurium in hydrochloric acid is mixed with boiling water, and left to cool slowly. (Berzelius.)

Properties.—When prepared by method (1) it forms a crystalline crust, consisting of octohedrons, which may be distinguished by the microscope; it is colourless while moist, and milk-white when thoroughly dry. That prepared by (3) forms octohedrons, distinguishable by the naked eye. Organic matter, which is very readily taken up by tellurous acid, gives it a pale yellow colour. When tellurous acid thus contaminated is heated in a glass tube, it blackens, emits slight fumes, and then becomes colourless. When slightly heated, it turns yellowish; a stronger heat causes it to assume, for the time, an orange-yellow colour. At an incipient red heat, it fuses into a transparent, dark-yellow liquid, which, on exposure to the air, volatilizes with emission of slight fumes. On cooling it solidifies, evolving sufficient heat to raise it again to low redness, and forms a white, highly crystalline mass, translucent when very slowly cooled, which easily separates from the crucible, and may be broken by the fingers into crystalline fragments. Single drops often solidify to a transparent glass. Volatilizes and sublimes, but at a temperature much higher than the subliming point of the metal, in the form of a soft mealy powder: it may, therefore, be fused in a covered crucible without much loss. The powder reddens moist litmus-paper, but not till after some time; it is tasteless at first, but afterwards excites an unpleasant metallic taste.

	Calculation.		Berzelius.	Klaproth.
Te	64	80	80·04	83·14
2O	16	20	19·96	16·86
TeO^2	80	100	100·00	100·00

Decomposed by charcoal at a comparatively low temperature, with a kind of detonation. On charcoal before the blowpipe, it is decomposed with effervescence, the flame exhibiting a green colour, and the greater part of the tellurium evaporating: part of the metal however burns again, and is reconverted into telluric oxide, which forms a white deposit on the charcoal. Slowly reduced by hydrogen gas, at a temperature not lower than that at which the metal sublimes. If selenious acid is likewise present, a red mealy powder is deposited in the tube. (Berzelius.)

Combinations.—*a.* With Water.—*α. Hydrate of Telluric Oxide* or *Hydrate of Tellurous Acid.*—1. Formed by precipitating a solution of tellurium in nitric acid of specific gravity 1·25, with water.—2. By fusing dry tellurous acid with an equal weight of carbonate of potash, dissolving the resulting tellurite of potash in cold water, and adding nitric acid in scarcely perceptible excess. The mixture is set aside for a considerable time, and stirred frequently, so that no tellurite of potash may remain undecomposed, and the tellurous acid thrown on a filter.—3. By dissolving dry tellurous acid in caustic potash, and proceeding in the same manner. The acid thus obtained is washed with ice-cold water, and dried in the air at a temperature below 12°. (Berzelius.)

White voluminous flakes, which are earthy after drying, instantly redden moist litmus-paper, and have a sharp metallic taste. At 40°, and frequently even at lower temperatures, the hydrate is resolved into grains of anhydrous tellurous acid, so that a milky mixture of it with water is converted into a clear liquid, containing crystalline grains of the dry acid. (Berzelius.)

β. Aqueous Tellurous Acid.—The dry acid dissolves but very sparingly in water, forming a tasteless liquid, which does not redden litmus, and, on evaporation, leaves the acid in the form of a finely pulverulent film. The hydrate dissolves in water with tolerable facility. The solution redden litmus, and has a metallic taste: when heated above 40°, it becomes milky and loses its power of reddening litmus, because it then deposits the anhydrous acid in the form of fine grains: when freely evaporated, it leaves the anhydrous acid, together with a small quantity of the hydrate. (Berzelius.)

b. With Acids, forming the SALTS OF TELLURIC OXIDE OF TELLURIC SALTS.—Anhydrous telluric oxide dissolves but very sparingly in most acids; hydrochloric acid alone dissolves it somewhat more freely. The hydrate is easily soluble. The sulphate and nitrate are likewise obtained by treating the metal with the corresponding acids. Telluric salts are colourless, unless they contain a coloured acid; they have a disagreeable metallic taste, closely resembling that of antimonic salts (Berzelius); they are strongly emetic (Kölreuter). After ignition with potash and charcoal, they yield a red solution in water. (Berzelius.) Phosphorus precipitates metallic tellurium from these salts (Berzelius); phosphorus dissolved in alcohol gives a white precipitate, which soon turns black. (Fischer.) Sulphurous acid precipitates metallic tellurium. (Wehrle, *Zeitsch. Phys. Math.* 9, 138.) Hence a solution of sulphurous acid or bisulphite of ammonia, potash, or soda, forms a useful reagent for separating tellurium. To prevent the water in which the sulphurous acid and its salts are dissolved, from precipitating a basic salt of tellurium, which would then no longer be reduced, the solution must be strongly acidulated with hydrochloric acid. If the solution is cold, it remains transparent and colourless for a short time after mixing, but afterwards becomes brownish and turbid from precipitation of tellurium: if it is warm, a turbid mixture is immediately produced, blue by transmitted and green by reflected light. The warmer and stronger the solution, the more quickly and completely is the precipitation effected. In the cold, the precipitation is never complete, even if the sulphurous acid is in excess; hence fresh turbidity is produced on heating the liquid; but if the solution be heated for a long time in the air, the excess of sulphurous acid will be driven off, and then the tellurium may be oxidized by the air and redissolved; towards the end of the process, therefore, sulphite of potash must be added in excess, and the liquid heated till it boils. If the tellurium-solution contains nitric acid, the metal is still precipitated, but redissolves with evolution of nitric oxide. If the liquid contains selenious acid, selenium is precipitated together with the tellurium. Certain metals also, which, when alone, are not reduced by sulphurous acid, are, nevertheless, precipitated in company with the tellurium,—*e. g.*, silver and gold completely, bismuth and copper in small quantity, iron in still smaller quantity. In washing the precipitated tellurium, the filter must be kept constantly full of the liquid, as otherwise the tellurium will oxidate, and be dissolved by the acid still present. It is, therefore, advisable to concentrate the filtrate by evaporation, and then treat it with sulphite of ammonia, in order to precipitate any tellurium that may have been dissolved.

Tellurium is precipitated in the metallic state by zinc, tin, antimony (Klaproth), iron, copper (Berzelius), cadmium, lead, and mercury. (Fischer.) It is generally precipitated in the form of a black powder, which acquires metallic lustre by rubbing; lead however precipitates it in the dendritic form. It is difficult to ensure complete precipitation: towards the end of the reaction, a basic salt of tellurium is often precipitated, or a compound of tellurous acid with the oxide of the other metal. (Fischer, *Pogg.* 12, 502.) Protochloride of tin and green vitriol precipitate the tellurium in the metallic state. The former gives a black fibrous precipitate, and, if the solution is very dilute, colours it brown after a while: this colour is still apparent when only 1 part of telluric oxide is contained in 60,000 parts of the liquid. Green vitriol does not precipitate tellurium, unless the telluric salt is perfectly neutralized, and of a particular degree of concentration. (Fischer, *Pogg.* 13, 257.)

The solutions of tellurium in inorganic acids (not those which contain vegetable acids), provided the acid is not in very great excess, yield, when largely diluted with water, a white precipitate, consisting partly of hydrated telluric oxide, partly of a basic salt, from which the remaining portion of acid may be extracted by repeated washing with warm water; the dilute acid above the precipitate retains but a small quantity of telluric oxide in solution.—Caustic ammonia, potash, and soda, and likewise their monocarbonates and bicarbonates precipitate the hydrated oxide in thick white flakes, which dissolve completely in excess of the alkali (in the alkaline carbonates, however, only on the application of heat).—Phosphate of soda gives a white precipitate.—Hydrosulphuric acid and hydrosulphate of ammonia throw down black-brown sulphide of tellurium, easily soluble in excess of the alkaline hydrosulphate.—Acetate of lead and nitrate of mercurous oxide give, according to Fischer, a white precipitate; an ammoniacal solution of oxide of copper gives a greyish-blue precipitate.—Tincture of galls throws down cream-coloured flakes.—No precipitate is produced by oxalic acid, or by ferrocyanide or ferricyanide of potassium.

c. With Salifiable bases, forming the SALTS OF TELLUROUS ACID; TELLURITES. The tellurites of the soluble alkalis may be formed by direct combination, either in the dry or in the moist way. Anhydrous tellurous acid dissolves very slowly in aqueous ammonia, easily in aqueous potash or soda, and only by continued boiling in aqueous carbonate of potash or soda: it may, however, be easily fused with carbonate of potash or soda, carbonic acid being driven off. The hydrated acid dissolves readily in warm aqueous solutions of the caustic alkalis or their carbonates; the latter are thereby converted into bicarbonates, the carbonic acid not escaping unless heat is applied. The other salts of tellurous acid are obtained either by fusion or by precipitating the aqueous solution of an alkaline tellurite with a salt of the less soluble alkalis, or of the earths or heavy metallic oxides.—The tellurites contain 1 atom of base with 1, 2, or 4 atoms of acid. They are fusible, and generally solidify in the crystalline form on cooling; the quadrotellurites, however, form a glass. Tellurites are colourless unless they contain a coloured base; those which are soluble have a metallic taste. Most of them, when heated to redness with charcoal, yield metallic tellurium, sometimes with slight detonation: the reduced metal, if roasted in an open tube, yields a sublimate of tellurous acid. These salts, when reduced on charcoal before the blowpipe, impart a green colour to the flame. When ignited with potassium, or with charcoal and carbonate of potash, they yield telluride of potassium, which dissolves in water, forming a wine-red solution. With the tellurites of zinc, silver, and a few others, this reaction does not take place. The tellurites of ammonia, potash, and soda are easily soluble in water; those of baryta, strontia, and lime are difficultly soluble; and those of the earths and heavy metallic oxides insoluble. An aqueous solution of a tellurite is decomposed even by the carbonic acid of the air. Nearly all tellurites dissolve in strong hydrochloric acid, and without evolving chlorine on the application of heat; the solution exhibits the reactions of a salt of telluric oxide, except in so far as those reactions may be interfered with by the presence of a stronger base. (Berzelius.)

B. TELLURIC ACID. TeO^3.

Formation.—1. By fusing tellurous acid with nitrate of potash.—2. By the action of chlorine on tellurite of potash.—3. In small quantity, when tellurium is dissolved in nitric acid. (Berzelius.)

Preparation.—1. One part of tellurous acid is fused with 1 part of carbonate of potash (or soda), the fused mass dissolved in water, and at least 1 part of caustic potash added to the solution; or tellurous acid is dissolved in about twice the quantity of caustic potash required to neutralize it completely. Through the solution of basic tellurite of potash obtained by one of these methods, chlorine gas is passed till the precipitate which is at first produced is completely redissolved, and the liquid smells of chlorine. A few drops of chloride of barium are then added, to precipitate any sulphuric or selenic acid that may be present; the liquid filtered, in case of any precipitate being thereby produced; the solution supersaturated with ammonia; and chloride of barium added as long as tellurate of baryta continues to be precipitated. The precipitate, which is very bulky when first formed, ought quickly to aggregate in crystalline grains; if this change does not take place, the precipitate likewise contains tellurite of baryta. The precipitate is then dried at a gentle heat; 4 parts of it digested with 1 part of oil of vitriol and from 4 to 8 parts of water; the filtrate concentrated to a certain extent in the water-bath; and then left to crystallize by spontaneous evaporation. The acid may likewise be separated, though less advantageously, by dissolving the tellurate of baryta in dilute nitric acid; precipitating the baryta by sulphuric acid; evaporating the filtrate to dryness in the water-bath, in order to drive off the nitric acid; dissolving the residue in water; and crystallizing by spontaneous evaporation. The best crystals are obtained when sulphuric acid is present. To free the crystals from adhering sulphuric acid, they are either pounded and washed with alcohol;—or their aqueous solution is evaporated to dryness in the water-bath; the residue exposed to the same degree of heat for some hours; then left to cool, and exhausted with cold water, which extracts scarcely anything but the sulphuric acid; the residue dissolved in boiling water, which leaves tellurous acid undissolved; and the filtrate left to evaporate spontaneously. The liquid, after being treated with chlorine, may likewise be mixed with a boiling solution of chloride of lead: the telluric acid will then be precipitated in the form of tellurate of lead; and the precipitate, after thorough washing, may be decomposed by hydrosulphuric acid in the manner described under (2).

2. A mixture of tellurous acid and nitre is heated, with constant stirring, till the mass, which at first assumes a dark red colour, is converted into a transparent and colourless liquid. The heat applied must not be more than sufficient to bring the bottom of the crucible to dull redness, because a higher temperature would reconvert the tellurate of potash into tellurite. From the resulting mass, when cooled and pulverized, cold water extracts nitrate, tellurite, and tellurate of potash. The bitellurate of potash which remains undissolved, is taken up by boiling water, and the solution neutralized with ammonia, and precipitated either by chloride of barium or nitrate of lead. The tellurite of baryta is treated as in method (1). The tellurate of lead, after washing, is either decomposed, like the tellurate of baryta, by sulphuric acid; or—since telluric acid is not immediately decomposed by hydrosulphuric acid at ordinary temperatures—the tellurate of lead may be diffused in water; quickly decomposed by a stream of hydrosulphuric acid gas, continued till the liquid smells of it after being shaken up; the excess of that acid quickly removed by the addition of a portion of tellurate of lead set apart for that purpose; and the liquid filtered and evaporated. (Berzelius.) The crystallized acid obtained by one of these methods is converted into

the anhydrous acid by heating it not quite to redness. If any portion of the telluric acid has been converted into tellurous acid by the application of too much heat, the tellurous acid may be dissolved out by hydrochloric acid. (Berzelius.)

Properties.—Orange-yellow mass, having the form of crystals.

	Calculation.		Berzelius.
Te	64	72·73	72·77
3O	24	27·27	27·23
TeO^3	88	100·00	100·00

Decompositions.—At a temperature much below the melting point of tellurous acid, telluric acid is resolved into oxygen gas and white pulverulent tellurous acid. Strong hydrochloric acid decomposes telluric acid slowly and only with the aid of heat, the products of the reaction being chlorine gas and hydrochlorate of telluric oxide.

Combinations.—*a.* With Water.—*α. Hydrate of Telluric Acid.*—Formed by heating the crystallized acid to 160°. The crystals are converted, without change of form, into an opaque mass, which is yellow while hot, but turns white on cooling.

	Calculation.		Berzelius.
TeO^3	88	90·72	90·74
HO	9	9·28	9·26
HO,TeO^3	97	100·00	100·00

β. Crystallized Telluric Acid.—Formed by spontaneous evaporation of the aqueous solution. Colourless, tolerably large, flattened, six-sided prisms, with very obtuse four-sided summits (somewhat like *Fig.* 67), and often longitudinally striated; or—if they separate from a solution containing sulphuric acid, or from a warm concentrated solution—very short eight-sided prisms. Reddens litmus slightly. Taste not sour but metallic, very much like that of nitric acid. The crystals retain their 3 atoms of water at 100°; at 160°, they give off 15·6 per cent. (2 atoms) and leave the hydrate *α*; at a stronger heat, but below redness, they give off the remaining 7·9 per cent. (1 atom) of water and leave the anhydrous acid, which, at a higher temperature, gives off 7 per cent. of oxygen and leaves 69·5 per cent. of tellurous acid:

	Calculation.		Berzelius.
TeO^3	88	76·52	76·5
3HO	27	23·48	23·5
$3HO,TeO^3$	115	100·00	100·0

γ. Aqueous Telluric Acid.—The anhydrous acid is perfectly insoluble even in boiling water, and when thrown into water in the state of fine powder, merely diffuses itself through the liquid, producing a yellow milkiness. The hydrated acid dissolves easily in hot water, and very slowly, though completely, in cold water. The crystallized acid dissolves slowly but abundantly in cold water. One part of the acid dissolves in 1·63 pt. water at 19·5°, and in boiling water in almost any proportion. The solution evaporated to a syrupy consistence in the water-bath solidifies in the crystalline form on cooling; when evaporated to dryness in the water-bath, it leaves a milk-white, amorphous mass, which, if digested in water, after cooling, first separates in translucent flakes and then dissolves very slowly. The aqueous solution saturated with hydrosulphuric acid deposits tersulphide of tellurium, slowly in the cold, more quickly when heated. From the saturated aqueous solution, strong alcohol precipitates part of the telluric acid.

Telluric acid does not combine with other acids; the anhydrous acid is insoluble in cold hydrochloric and in hot nitric acid.

b. With Salifiable Bases, telluric acid forms salts called TELLURATES. Telluric acid has but slight affinity for bases. The hydrated acid withdraws from aqueous solutions of alkaline carbonates, only so much alkali as to form a salt containing 2 atoms of acid. The anhydrous acid is insoluble in boiling potash, unless the latter is so concentrated as to solidify on cooling. Telluric acid forms bibasic, sesquibasic, monobasic, bi-acid, and quadracid salts. They are all colourless, unless the base is coloured. The alkaline monotellurates have a caustic alkaline taste; the bitellurates of the same bases have an alkaline reaction, and taste partly alkaline, partly metallic. At a red heat, tellurates are converted into tellurites, at the same time fusing, assuming a yellow or brown colour, and evolving oxygen gas. Many alkaline quadrotellurates which, in the hydrated state, are colourless and soluble in water, give off water when heated, even short of redness, and pass into a peculiar state in which they are yellow and insoluble in aqueous acids and alkalis. Hence Berzelius assumes the existence of two isomeric modifications of telluric acid—the insoluble modification occurring in anhydrous telluric acid and in the de-hydrated yellow salts just mentioned, and the soluble variety in the hydrated acid and the ordinary tellurates. Many tellurates, when heated on charcoal before the blowpipe, yield metallic tellurium, the reduction being generally attended with slight detonation. The reduced tellurium, if roasted in an open tube, yields a sublimate of tellurous acid. Most tellurates, when ignited with potassium or with a mixture of charcoal and carbonate of potash, yield a mass which gives up telluride of potassium to water, and thereby colours it wine-red. Most acids, even acetic acid in excess, abstract the base of the alkaline tellurates; the aqueous solutions of these salts give a precipitate with tincture of galls. Solutions of tellurates in cold concentrated hydrochloric acid are not yellow and give no precipitate with water; but when heated, they evolve chlorine, thereby becoming yellow, and—if the acid is not in very great excess—precipitable by water: the hydrochloric acid solution heated with sulphurous acid, deposits metallic tellurium. The tellurates of the more soluble alkalis dissolve in water with tolerable facility, the quadrotellurates being the least soluble: hence a small quantity of alkali added to the aqueous acid produces a precipitate which dissolves in a larger quantity of the alkali. The tellurates of the earthy alkalis are but slightly soluble, those which contain 2 or 4 atoms of acid being, however, more soluble than the simple salts. The tellurates of the earths and heavy metallic oxides are almost insoluble; nevertheless, water extracts from some of them an acid salt and leaves a basic salt undissolved. The aqueous solutions of the more easily soluble tellurates give with chloride of barium a precipitate which is bulky at first, but afterwards becomes granular, and is soluble in hydrochloric or nitric acid. (Berzelius.)

Crystallized telluric acid is insoluble in absolute alcohol, slightly soluble in hydrated alcohol.

TELLURIUM AND HYDROGEN.

Ritter (*Gilb.* 29, 148) has shown that when the negative electricity of a voltaic circuit is conducted into water by means of tellurium, no hydrogen is evolved on the metal, but a *Hydride of Tellurium* is formed, having strong colouring properties. Sir H. Davy (*Gilb.* 37, 49) found that the water surrounding the tellurium acquired a purple tint, from formation of hydrotelluric acid; and that, by access of air, a brown powder was precipitated, which he regarded as a compound of tellurium with a smaller quantity of hydrogen, *i.e.* as hydride of tellurium. But according to Magnus (*Pogg.* 17, 521), this brown powder is nothing but metallic tellurium, and there is no such thing as a hydride of that metal. The brown powder is precipitated even when thoroughly boiled water is used, because the oxygen evolved at the positive pole diffuses itself through the liquid. If the water contains an acid, no brown powder is deposited, because the hydrotelluric acid which is then produced, being but slightly soluble in acid liquids, immediately escapes as gas. (Magnus.)

HYDROTELLURIC ACID. HTe.

Telluretted Hydrogen, Hydrotellursäure, Hydrotellurgas, Tellurwasserstoffsäure, Tellurwasserstoffgas, Acide hydrotellurique, Acide tellurhydrique, Gas hydrogène telluré.

Preparation.—By digesting telluride of potassium (H. Davy), or telluride of zinc, or telluride of iron (Berzelius) in a gas-generating vessel with hydrochloric acid; the gas is received over mercury.

Properties.—Colourless gas, having a disagreeable and peculiar odour, very much like that of hydrosulphuric acid. When newly prepared, it reddens litmus; but loses this property by washing with water, either because the air in the water decomposes the gas, or because the water withdraws the hydrochloric acid mixed with it. (H. Davy.) Specific gravity = 4·489 (Bineau, *Ann. Chim. Phys.* 68, 424.)

Te	64	98·46
H	1	1·54
HTe	65	100·00

	Vol.	Sp. gr.		Vol.	Sp. gr.
Tellurium vapour	1	26·6112	=	⅙	4·4352
Hydrogen gas	6	0·4158	=	1	0·0693
Hydrotelluric acid gas	6	27·0270	=	1	4·5045

Decompositions.—1. The gas, when in contact with air, takes fire on the approach of a burning body and burns with a bluish flame, forming water and telluric oxide. (H. Davy.)—2. Chlorine mixed with the gas immediately precipitates tellurium, which is soon converted into chloride of tellurium. (H. Davy.)—3. Heated tin decomposes the gas, withdrawing the tellurium and leaving hydrogen gas of the same volume as the hydrotelluric acid. (Bineau.)—4. The gas is decomposed by contact with various heavy metallic oxides dissolved in acids, yielding water and a metallic telluride. (Berzelius.)

Combinations.—*a.* With water.—*Solution of Hydrotelluric Acid.*—Water absorbs the gas, forming a pale red liquid, which, when exposed to the air, turns brown and deposits metallic tellurium. (H. Davy.)

b. With the soluble alkalis, forming *Alkaline Hydrotellurates*, which may likewise be regarded as tellurides of the alkali-metals, *e.g.* $KO,HTe = KTe + HO$.

Tellurium and Phosphorus.

Phosphate of Telluric Oxide.—White powder, insoluble in water. (Berzelius.)

Tellurium and Sulphur.

A. Sulphide of Tellurium.—Tellurium and sulphur may be melted together in all proportions. Sulphur with a small quantity of tellurium forms a yellowish-red mixture; with a larger quantity, a substance which is red by transmitted and black by reflected light; and with a still larger quantity, an opaque, lead-grey mixture. (Berzelius.)

a. Bisulphide, Tellurous Sulphide, Sulphotellurous Acid.—1. Formed by passing hydrosulphuric acid gas through the solution of a salt of telluric oxide.—2. By passing hydrosulphuric acid through a solution of an alkaline tellurite till that salt is converted into a sulphotellurite of the alkali-metal, and then precipitating by an acid. The precipitate produced by either of these methods, which is at first flocculent, brown, and translucent, soon becomes darker, indeed almost black.—3. By exposing a sulphotellurite of an alkali-metal to the air. In this case, the bisulphide of tellurium is precipitated in the form of a non-crystalline film, destitute of metallic lustre. (Berzelius.)

Brown-black; under the burnishing steel, it acquires the metallic lustre and a lead-grey colour. Softens when heated, but without melting completely; swells up; and, on cooling, solidifies to a blistered, grey mass, which has a semi-metallic lustre, is easily pulverized, and does not conduct electricity. When heated in a retort somewhat strongly and for a considerable time, it is decomposed, yielding a distillate of sulphur—which, from admixture of a small quantity of tellurium, is coloured dark-red at first and afterwards black—and a residue of tellurium perfectly free from sulphur. If the sulphide of tellurium is mixed with a small quantity of another metallic sulphide, the latter also gives up its sulphur, so that a metallic telluride is left behind. Bisulphide of tellurium dissolves slowly but completely in boiling potash or soda, forming a deep yellow solution; when freshly precipitated, it likewise dissolves sparingly in strong solution of ammonia, to which it imparts a pale yellow tint; the ammonia readily dissolves out any sulphide of arsenic that may be mixed with it. (Berzelius.)

Te	64	66·67
2S	32	33·33
TeS^2	96	100·00

With basic metallic sulphides, bisulphide of tellurium forms compounds called *Sulphotellurites.* Those of the alkali-metals and magnesium are most readily obtained by saturating the solution of an alkaline tellurite with hydrosulphuric acid gas. If, however, a monotellurite of the alkali be used for the purpose, two-thirds of the resulting tellurous sulphide is precipitated, because 3 atoms of an alkaline sulphide dissolved in water can only take up 1 atom of the tellurous sulphide: such at least is the relation in the sodium-compound, which is composed of $3NaS,TeS^2$. It is true that the sulphur-salt, after evaporation to dryness, may be fused with a larger quantity of tellurous sulphide, but the excess is left behind on digesting the fused mass in water. From alkaline bihydrosulphates, sulphotellurous acid drives out the excess of hydrosulphuric acid on boiling, and forms the same solution as above; the higher sulphides of the alkali-metals are but slowly and imperfectly decomposed by it. These compounds, mixed with an alkaline tellurite, are obtained on dissolving bisulphide of tellurium in caustic potash or soda; probably thus:

$$9KO + 5TeS^2 = 3(KO,TeO^2) + 2(3KS,TeS^2).$$

The sulphotellurites of the earth-metals and heavy metals are obtained by double decomposition.

The anhydrous sulphotellurites of the alkali-metals are brownish yellow; the crystallized hydrates and the aqueous solutions pale yellow. The anhydrous sulphotellurites of the alkali-metals may be ignited without decomposition out of contact of air, and, at ordinary temperatures, remain unaltered when exposed to the air. In the state of solution they are quickly decomposed, the alkaline sulphide being converted into a hyposulphite, while the bisulphide of tellurium separates in the form of a grey metallic film on the surface of the liquid. The alkaline sulphotellurites are easily soluble in water, less easily in alcohol; in the latter case, sulphide of tellurium is deposited, and the liquid acquires a deep yellow colour. Acids added to the solutions of these salts throw down bisulphide of tellurium. The sulphotellurites of the heavy metals, when ignited in close vessels, are, for the most part, decomposed, the sulphide of tellurium giving up its sulphur, and the tellurium either combining with the whole of the more basic metal and separating the whole of the sulphur—or with only a part of it,—so that the residue consists, either of metallic telluride alone, or of a mixture of that compound with the basic sulphide. (Berzelius.)

Tersulphide of Tellurium, Telluric Sulphide, Sulphotelluric Acid.—A dilute aqueous solution of telluric acid, saturated with hydrosulphuric acid gas, and set aside in a closed vessel in a warm place, turns brown without losing its transparency; but afterwards loses its colour, and deposits tersulphide of tellurium, which covers the sides of the vessel in the form of a blackish-grey, metal-shining film, easily rubbed off in flakes. The compounds of this sulphide with the more basic metallic sulphides — the *Sulphotellurates* — have not been further examined. (Berzelius.)

c. Tetrasulphide of Tellurium.—Tellurium and sulphur, melted together in equal parts, yield a lead-coloured, radiated mass. (Klaproth.)

B. *Sulphate of Tellurous Oxide?*—Tellurium immersed in 100 parts of oil of vitriol, at ordinary temperatures, imparts a fine amethyst colour to the liquid; a small quantity of water added to the solution destroys the colour, precipitating brown-black flakes of metallic tellurium. (Müller von Reichenstein, Klaproth.)—Anhydrous sulphuric acid, sealed up in a tube with tellurium-powder, produces a red colour at a few points only, probably arising from moisture; otherwise it remains colourless for a considerable time, even if melted. But if, in consequence of the air not being perfectly excluded, the sulphuric acid should absorb a trace of water, it dissolves the tellurium in large quantity producing a red colour, and giving off sulphurous acid. The solution contains 1 part of tellurium to 9·4 parts of acid; on the addition of water, 0·9 pt. falls down in the metallic state, while 0·1 remains in solution as oxide.—Pounded tellurium dissolves in cold fuming oil of vitriol in the proportion of 1:48, the solution smelling perceptibly of sulphurous acid, even if the moisture of the air be completely excluded. Oil of vitriol which does not fume, dissolves only $\frac{1}{2000}$ tellurium, and without perceptible odour of sulphurous acid. With oil of vitriol moderately warmed, tellurium forms a darker solution, having a stronger violet colour. The metal continues to dissolve, and the violet colour to increase, so long as the oil of vitriol does not boil; but when ebullition commences, the solution loses its colour, and sulphate of telluric oxide is formed. The red solution probably contains a lower oxide of tellurium, which, on the addition of water, is partly reduced to the metallic state by the sulphurous acid still present, and is partly resolved into metallic tellurium and telluric oxide, which remains in solution. (N. W. Fischer, *Pogg.* 12, 153; 15, 77; 16, 118.) The red solution, when preserved in close vessels, remains unaltered for a long time; when exposed to the air, it absorbs moisture and becomes decolorized, the tellurium being converted into TeO^2, at the expense of the sulphuric acid: hence the liquid, when exposed to the air, smells constantly of sulphurous acid. But the odour of sulphurous acid is not perceived at the time of dissolving the metal in oil of vitriol; consequently, the red solution contains metallic tellurium in direct combination with sulphuric acid, corresponding to the solution of sulphur and selenium in sulphuric acid. (Magnus, *Pogg.* 10, 491.) The theory of Magnus is supported by the red colour of the solution, which agrees with that of telluride of potassium in water. (Berzelius.)

C. Sulphate of Telluric Oxide or Telluric Sulphate.—*a. Basic Sulphate.*—Formed by heating the dry salt, *b*, in a retort, till part of the sulphuric acid is driven off; there then remains an easily fusible, vitreous residue, which is yellow while fused, and becomes transparent and colourless on cooling; when more strongly heated in an open crucible, it gives off all its sulphuric acid, leaving fused telluric oxide, which solidifies in an opaque crystalline mass. (Berzelius.)

b. Bisulphate.—Pounded tellurium made into a thin paste with oil of vitriol, yields, when heated, a purple-red mass, which, as soon as all the liquid is driven off, evolves sulphurous acid and becomes colourless. After the expulsion of the oil of vitriol, there remains a white, earthy mass, having at first a drying and afterwards a metallic taste. When heated to redness, it melts and leaves a residue, first of salt *a* and afterwards of telluric oxide. Water resolves it into telluric oxide and dilute sulphuric acid containing a very small quantity of oxide in solution. It dissolves in warm hydrochloric or nitric acid, and, if the solution be saturated, separates from it in grains on cooling. (Berzelius.)—When 1 At. tellurium-powder is dissolved in 1 At. sulphuric acid diluted with water, heat being applied and strong nitric acid added, a large quantity of anhydrous tellurous acid separates from it on cooling; and if the liquid be poured off and the excess of nitric acid evaporated, pearly scales of the bi-acid salt are obtained. (Berzelius.)

When tellurium is heated with excess of oil of vitriol, till the red solution becomes decolorized by boiling, a salt which is easily soluble in water, separates on cooling. The supernatant liquid slowly dissolves tellurium, forming a red solution, and is slightly reddened, even after some time, by the introduction of a rod of zinc. (Fischer.)—Tellurium dissolves in oil of vitriol mixed with 2 or 3 parts of water and a small quantity of nitric acid, forming a colourless liquid which is not decomposed by the addition of a larger quantity of water. (Klaproth.)

Tellurium and Selenium.

Selenide of Tellurium.—These two bodies may be fused together in all proportions. They evolve heat in uniting, and form an iron-black brittle mass, of crystalline fracture; this substance fuses to a thin liquid, even below a red heat; boils at a higher temperature; evaporates undecomposed out of contact of air; but when exposed to the air, readily oxidizes, and forms transparent drops, which appear to consist of telluric selenite. (Berzelius.)

Tellurium and Iodine.

Tellurium and iodine unite in all proportions.

A. Subiodide of Tellurium.—By heating the compound *b*, or by fusing a large quantity of tellurium with a small quantity of iodine, a metallic mass is obtained. (Berzelius.)

B. Proto-iodide of Tellurium.—*Tellurous Iodide, Iodotellurous Acid.*—TeI.—Formed by heating in a distilling apparatus a pounded mixture of 1 At. tellurium, and rather more than 1 At. iodine, at a very gentle heat. The excess of iodine passes off, and the proto-iodide of tellurium sublimes in black, crystalline flakes, having some metallic lustre, very fusible and volatile, and forming, after fusion, a mass which has a non-crystalline fracture.—When suddenly heated, it gives off iodine and is converted into A.—When digested in aqueous hydrochloric acid or ammonia, it finally leaves a residue of metallic tellurium. It is not attacked by water, even when boiling. (Berzelius.)

C. Biniodide of Tellurium.—*Telluric Iodide, Iodotelluric Acid.*—Formed when finely pounded hydrate of telluric oxide is digested in a closed vessel for some time, with aqueous hydriodic acid. The telluric oxide is then converted into coherent, iron-grey biniodide of tellurium. A small quantity of this compound dissolves in the excess of hydriodic acid, imparting to it a dark brown colour, and may be separated from it in iron-grey prisms, by evaporation in vacuo over oil of vitriol and burnt lime, which takes up the hydriodic acid and excess of iodine. When tellurium-powder is digested for a considerable time with iodine and water, the dark brown liquid poured off from the insoluble portion contains but a small quantity of biniodide of tellurium dissolved in excess of iodine; on evaporation, it gives off iodine, becomes continually paler, and leaves a black residue of biniodide of tellurium.

Fine, nearly black grains, or iron-grey prisms.

Te	64	20·25
$2I$	252	79·75
TeI^2	316	100·00

Biniodide of tellurium fuses when heated, and on boiling evolves iodine, pure at first, but becoming continually richer in tellurium, till the compound A is left behind.—By water it is resolved into tellurite of telluric iodide which retains the form of the telluric iodide, and aqueous hydriodic acid in which a small quantity of the telluric iodide dissolves. (Berzelius.) Cold water exerts but a slight decomposing action, and remains colourless, taking up, however, a small portion of hydriodic acid; boiling water acquires a dark brown colour; after thorough boiling with water, 100 parts of telluric iodide leave 23·5 parts of the tellurite of that compound. The brown solution, when evaporated, evolves hydriodic acid and iodine, leaving behind the dissolved biniodide. (Berzelius.)

$$3TeI^2 + 4HO = TeI^2, 2TeO^2 + 4HI.$$

Hence, 3 At. TeI^2 (=948 parts) should give up $\frac{2}{3}$ of its iodine as hydriodic acid, and yield 1 At. $TeI^2, 2TeO^2$ (=376 parts); 948 : 376=100 : 39·66; consequently, 100 parts of telluric iodide should yield 39·66 parts of the tellurite; but as a small quantity of the biniodide dissolves in the aqueous hydriodic acid, the quantity actually obtained is only 36·5 parts.—Biniodide of tellurium dissolves in alcohol, undergoing, however, some decomposition, even when the alcohol is absolute. (Berzelius.)

Biniodide of tellurium combines with other metallic iodides, especially with those of the alkali-metals. These compounds, which may be called *Iodotellurates*, are obtained by exactly saturating a solution of telluric iodide in concentrated hydriodic acid with an alkali, or by mixing it with an alkaline hydriodate and leaving the mixture to spontaneous evaporation. On the other hand, solid telluric iodide is but slightly soluble in aqueous-alkaline hydriodates. Iron-grey, shining crystals, forming with a small quantity of water, a brown solution which is but slightly precipitated by a larger quantity of water.

D. TELLURITE OF TELLURIC IODIDE.—Formed by boiling biniodide of tellurium with successive quantities of water. Pale greyish-brown, very heavy. Fuses with difficulty when heated, yielding traces of water, then iodine mixed with a very small quantity of tellurium, and lastly, at a strong red heat, a sublimate of metallic tellurium which collects in drops. This compound is not decomposed by water. (Berzelius.)

E. HYDRIODATE OF TELLURIC IODIDE.—Concentrated hydriodic acid saturated with biniodide of tellurium and evaporated in vacuo over oil of vitriol and slaked lime, yields long, right-angled, four-sided prisms, having the metallic lustre. These crystals, when sealed up in a glass tube and heated by the hand, melt into a dark brown liquid, which solidifies again on cooling. In an open vessel at 50° or 60°, they do not fuse, but give off a brown fume of hydriodic acid decomposed by contact with the air, and leave biniodide of tellurium having the form of the crystals but a dull surface and porous texture. Water decomposes the crystals, yielding a precipitate of telluric iodide, together with dilute hydriodic acid containing a small quantity of iodide of tellurium in solution, which gives it a brown colour. (Berzelius.)

F. TERIODIDE OF TELLURIUM or HYDRIODATE OF TELLURIC ACID.—Aqueous telluric acid forms with aqueous hydriodic acid, a mixture which is clear and brown at first, even if the latter predominates. This compound, when it evaporates spontaneously, deposits telluric iodide, while the excess of telluric acid collects in colourless prisms on the edge of the vessel. Hence one-third of the iodine goes off on evaporation. When telluric acid and hydriodic acid are mixed, in solutions saturated as completely as possible, biniodide of tellurium is immediately precipitated in the form of a black powder. (Berzelius.)

G. Periodide of Tellurium.—Formed by melting iodine in a glass tube, dropping in a piece of tellurium, shaking for a few seconds, and decanting to separate the iodine saturated with tellurium, from the tellurium which remains undissolved. Dissolves in water very slowly and sparingly, but gives it a very dark brown colour. The solution is decolorized by sulphite of ammonia, and, on the addition of hydrochloric acid, deposits metallic tellurium. (Berzelius.)

Tellurium and Bromine.

Bromine and tellurium combine at ordinary temperatures, the combination being attended with development of heat.

A. Sub-bromide of Tellurium.—Bibromide of tellurium may be fused with tellurium in any proportion.

B. Protobromide of Tellurium.—*Tellurous Bromide, Bromotellurous Acid.*—$TeBr$.—When a mixture of bromine and tellurium, containing an excess of the latter, is distilled, this compound passes over in the form of a violet vapour which condenses in fine black crystalline needles; these crystals fuse readily; and, on cooling, solidify in a mass, having a non-crystalline fracture and but little lustre. This compound is decomposed by water. (Berzelius.)

C. Bibromide of Tellurium.—*Telluric Bromide, Bromotelluric Acid.*—To form this compound, bromine is introduced into a glass tube sealed at one end and cooled by immersion in ice, pounded tellurium being afterwards added, not in excess, and with frequent stirring; the excess of bromine is driven off by the heat of a water-bath. Reddish yellow mass, which, when gently heated, fuses to a dark red, transparent liquid, and forms a crystalline solid on cooling; at a higher temperature, it is converted into a yellow vapour, which sublimes, partly in the form of a yellow meal, partly in pale-yellow crystalline needles.

Te	64·0	28·99
2Br	156·8	71·01
$TeBr^2$	220·8	100·00

Hydrated Bibromide of Tellurium, or *Bihydrobromate of Telluric Oxide.*—Bibromide of tellurium very slowly absorbs moisture when exposed to the air, and dissolves, without decomposition, in a small quantity of water. The yellow solution evaporated to a syrupy consistence over oil of vitriol, leaves dark ruby-red, rhombic tables, which, when more completely dried, give off their water and become yellow and earthy; they deliquesce very quickly when exposed to the air. The yellow solution, when mixed with a larger quantity of water, is resolved into precipitated tellurite of telluric bromide, and colourless, dilute hydrobromic acid containing a small quantity of telluric bromide in solution.

Bibromide of tellurium combines with the bromides of the alkali-metals, forming compounds which may be called *Bromotellurates.*

D. Tellurite of Telluric Bromide.—When bibromide of tellurium is decomposed by boiling water, and the liquid left to cool, a yellowish, granular compound crystallizes out, which, when heated, gives off the greater part of the telluric bromide, without intumescence, and after cooling leaves a yellow, crystalline mass. This mass, when ignited for a very long time, is converted into pure tellurous acid. The aqueous solution of telluric bromide heated with water till its colour is destroyed, and then evaporated over the water-bath, allows the hydrobromic acid to escape with the last portions of water, and yields a non-deliquescent, reddish-yellow varnish, which is rendered milk-white even by the smallest quantities of water. A larger quantity of water withdraws the bromine from the compound. (Berzelius.)

Tellurium and Chlorine.

A. Subchloride of Tellurium.—Protochloride of tellurium may be fused with tellurium in all proportions. Such a mixture, when ignited in a retort, first gives off protochloride of tellurium, then metallic drops of a compound richer in tellurium, and leaves a residue which resembles tellurium, but is more easily pulverized and reddens litmus; it must be freed from the chlorine still adhering to it, by fusion in an atmosphere of hydrogen, or by boiling the powder with a small quantity of hydrochloric acid and afterwards with water. (Berzelius.)

B. Protochloride of Tellurium.—*Tellurous Chloride, Chlorotellurous Acid.*—1. Formed by passing a gentle stream of chlorine gas over strongly heated tellurium or native telluride of silver, and freeing the distilled protochloride of tellurium from any bichloride that may be mixed with it—the former being the more volatile. The separation may also be effected, though less completely, by distillation over tellurium-powder. (H. Rose, *Pogg.* 21, 443.)—2. By mixing bichloride of tellurium with an equal weight of the metal, and collecting the protochloride by distillation. (Berzelius.) Black, amorphous body, having an earthy fracture and yielding a yellowish-green powder; it fuses readily to a black liquid, and is more volatile than C. Its vapour has the same colour as that of iodine, only paler (H. Rose); it is purple, but if air be completely excluded from the vessel, the colour somewhat inclines to yellow. (Berzelius.) It does not fume in the air. (H. Rose.)

				H. Rose.		
Te	64·0	....	64·38			
Cl	35·4	....	35·62	37·04	....	37·77
TeCl	99·4	....	100·00			

Attracts moisture from the air, and becomes surrounded with a drop of transparent liquid, which is rendered milky on the addition of water: with a larger quantity of water, a grey liquid is formed, tellurous acid and metallic tellurium being separated at the same time. When treated with aqueous sulphuric or hydrochloric acid, which retain the tellurous acid in solution, it deposits nothing but tellurium, in slender crystals, amounting to 32·04 per cent.—consequently half the quantity contained in the protochloride. (H. Rose.)

$$2TeCl + 2HO + xSO^3 = Te + TeO^2, 2HCl, xSO^3.$$

A mixture of tellurium and tellurous acid is separated even by triturating protochloride of tellurium with quick-lime or dry carbonate of soda. (Berzelius.) Protochloride of tellurium combines with sal-ammoniac.

Protochloride and bichloride of tellurium may be fused together in any proportion: if the former predominates, the compound is black, and opaque during fusion; if the latter is in excess, the compound is yellowish, and dark-red while liquid. (Berzelius.)

C. BICHLORIDE OF TELLURIUM.—*Telluric Chloride, Chlorotelluric Acid.*—Tellurium burns in chlorine gas with a white light, and is converted into white, easily fusible, and volatile telluric chloride. (H. Davy.) Chlorine gas does not act on tellurium at ordinary temperatures; but on the application of a gentle heat, combination takes place attended with combustion. The tellurium which still remains uncombined dissolves in the telluric chloride produced, and forms a black thick liquid which continues to absorb chlorine, at the same time becoming transparent and deep red, and ultimately deep yellow; on cooling, it acquires a lemon-yellow colour, and then solidifies to a white mass. A yellow tint after solidification would indicate the presence of protochloride. (Berzelius.) Bichloride of tellurium is snow-white, of crystalline texture, and fuses readily to a yellow liquid, which becomes deep red near the boiling point; boils at a stronger heat without spirting, and is converted into a deep yellow vapour, which, in dry air, condenses into a white, non-crystalline, mealy powder.

Te	64·0	....	47·47
2Cl	70·8	....	52·53
$TeCl^2$	134·8	....	100·00

The smallest quantity of organic matter causes the bichloride to turn yellow on melting, converting, in fact, a portion of that compound into protochloride, which then, at a higher temperature, escapes in violet vapours. Bichloride of tellurium when exposed to the air, deliquesces more rapidly than chloride of calcium, and is thereby converted into a thin liquid, which gradually turns milky, gives off hydrochloric acid, and dries up to a white residue, consisting of tellurite of telluric chloride. With boiling water it forms a clear solution, which, when slowly cooled, deposits crystals of tellurous acid mixed with smaller crystals of tellurite of telluric chloride. Combines with the chlorides of the alkali-metals, forming compounds which may be called *Chlorotellurates.*

D. TELLURITE OF TELLURIC CHLORIDE.—*Basic Telluric Chloride.*—*a.* Separates in the decomposition of telluric chloride by cold water. The whole of the chloride of tellurium may be separated by repeated washing, pure tellurous acid being left behind.—*b.* Crystallizes out from its solution in boiling water, together with tellurous acid. The crystals, when heated, evolve bichloride of tellurium, with strong decrepitation and intumescence; afterwards yield a small quantity of white sublimate, likewise consisting of tellurite of telluric chloride; and leave tellurous acid, which still contains telluric chloride, even after long ignition, and is therefore transparent when solidified, and fuses much more easily than pure tellurous acid.—*c.* Remains behind when bichloride of tellurium is exposed to the air till it has deliquesced and dried up again.—*d.* When a solution of tellurous acid is evaporated over the water-bath, there remains a pale yellow, transparent residue, which deliquesces very slowly, and at the same time becomes milk-white. (Berzelius.)—These compounds, *a*.... *c*, contain tellurous acid and bichloride of tellurium in various proportions. The calculations of their composition (*Pogg.* 32, 612–613), require revision, TeCl appearing therein instead of $TeCl^2$.

E. Hydrochlorate of Telluric Chloride, or Acid Hydrochlorate of Telluric Oxide.—1. Formed by dissolving telluric chloride, or telluric oxide, in hydrochloric acid.—2. By dissolving tellurium in aqua-regia.—The deep yellow solution, evaporated over the water-bath, leaves tellurite of telluric chloride, (*vid. sup.*) (Berzelius.)—If the solution does not contain a great excess of hydrochloric acid, the addition of water throws down tellurite of telluric chloride; an excess of water dissolves the precipitate (according to Fischer), only when the solution contains a considerable quantity of hydrochloric acid.

F. Hydrochlorate of Telluric Acid.—When a solution of telluric acid in strong hydrochloric acid is left to evaporate spontaneously, it gives off all its hydrochloric acid, and leaves pure telluric acid. (Berzelius.)

Tellurium and Fluorine.

A. Bifluoride of Tellurium.—*Telluric Fluoride.*—Sublimes on heating the compound B.—Transparent; solid at ordinary temperatures; soft or semifluid when heated; deliquesces very quickly in the air; deposits tellurous acid on the addition of a larger quantity of water.

B. Tellurite of Telluric Fluoride.—*a.* A solution of tellurous acid in aqueous hydrofluoric acid evaporated over the water-bath, yields a transparent and colourless syrup, which, on cooling, solidifies to a milk-white mass, consisting of little warty granules. When this mass is heated in a platinum crucible, over the mouth of which is placed a larger vessel of the same kind surrounded with water and ice, it melts, gives off water and afterwards hydrofluoric acid, and ultimately yields a sublimate of telluric fluoride.—*b.* After the mass has been heated to redness, there remains a compound of the same kind, richer in tellurous acid; this compound solidifies to a crystalline-granular mass, gives up hydrofluoric acid to boiling water, and evolves that acid when treated with oil of vitriol. (Berzelius.)

Tellurium and Nitrogen.

A. Nitrate of Telluric Oxide or Telluric Nitrate.—The metal dissolves easily in nitric acid, forming a colourless solution which is not decomposed by dilution with water. (Klaproth.) Water added to the solution precipitates the hydrate of tellurous acid in white flakes.—The solution, if left to itself at ordinary temperatures, or warmed for a quarter of an hour, deposits anhydrous tellurous acid in crystalline grains, so that the solution retains but a small quantity of tellurium, and is no longer decomposed by water.—When the solution is evaporated to dryness over the water-bath, there remains pure anhydrous telluric oxide, which, at higher temperatures, gives off only ½ per cent. more of oxygen. If the solution be left to itself for a while, the whole of the telluric oxide is deposited in the anhydrous insoluble state, and is then no longer precipitable by water. (Berzelius.)

B. BI-HYDROTELLURATE OF AMMONIA.—Ammoniacal gas mixed with hydrotelluric acid gas in excess, condenses in white crystalline laminæ, which at 80° are converted into a vapour whose density is 1·32. (Bineau, *Ann. Chim. Phys.* 67, 231; 68, 438.)—[There appears to be an error in Bineau's calculation of the vapour-density.]

C. TELLURITE OF AMMONIA.—*a. Monotellurite?*—The anhydrous acid dissolves very slowly in aqueous ammonia, the hydrated acid almost instantly. The monobasic salt cannot be obtained in the solid state from the solution; on evaporating the solution at a gentle heat, it gives off ammonia and leaves white crystalline grains containing 92·40 tellurous acid, 7·19 water, and 0·41 ammonia. Sal-ammoniac gives with the solution, a flocculent precipitate which appears to consist of the salt *b* (it is soluble in excess of ammonia, and does not reappear on the addition of sal-ammoniac); after washing with alcohol, it is no longer soluble in water.

b. Quadrotellurite.—1. If a solution of hydrated tellurous acid or bichloride of tellurium in warm aqueous carbonate of ammonia, be mixed while still warm with a small quantity of sal-ammoniac, a white, opaque, heavy, granular precipitate is slowly deposited.—2. Hereupon the addition of alcohol precipitates a further portion of the same salt.—When heated, it is resolved into ammonia, water, and tellurous acid.

	Dried at 60°.		Berzelius.	
			1.	2.
NH^3	17	4·45		
$4TeO^2$	320	83·77	83·1	83·87
$5HO$	45	11·78		
$NH^4O,4TeO^2+4Aq.$	382	100·00		

D. TELLURATE OF AMMONIA.—*a. Monotellurate.*—Cold aqueous ammonia forms with pulverized telluric acid, a white glutinous magma, which dissolves on boiling; the solution becomes turbid on cooling, but gradually resumes its transparency, and deposits white flakes and granules. Part of that which remains in solution may be precipitated by sal-ammoniac, and the rest by alcohol. The precipitate is washed with alcohol, which, however, exerts a slight solvent action as soon as the sal-ammoniac is washed away.—2. If a mixture of monotellurate of potash, sal-ammoniac, and a small quantity of ammonia, be dissolved in boiling water, and the solution left to cool, monotellurate of ammonia separates from it in the form of a crystalline crust.—The salt prepared by method (1) is white, and almost earthy after drying; it dissolves slowly, but completely, in cold water, quickly in boiling water. (Berzelius.)

b. Bitellurate.—Formed by precipitating a saturated solution of bitellurate of soda with sal-ammoniac. The solution of bitellurate of potash gives no precipitate, because it is less soluble in water.—The precipitate adheres to the glass in the form of a glutinous mass. It dissolves with difficulty in water. When boiled with water in open vessels, it gives off ammonia. If heated with water in close vessels, it partly melts to a white mass which solidifies on cooling, and partly dissolves in the water, separating in fine grains as the liquid cools. (Berzelius.)

c. Quadrotellurate.—1. By precipitating the solution of quadrotellurate of soda with ammonia. The addition of alcohol greatly increases the quantity of the precipitate, which may then be washed with alcohol. The salt is flocculent; when heated, it fuses imperfectly, swells up, and gives off water. It is but slightly soluble in water.—2. When a solution of monotellurate of ammonia is left to evaporate, either spontaneously or with the aid of a gentle heat, the quadrotellurate remains in the form of a gummy film, which becomes milk-white when moistened with water,—dissolves sparingly in cold, more abundantly in boiling water, the solution not yielding any deposit on cooling,—and turns yellow when carefully heated. (Berzelius.)

E. SULPHOTELLURITE OF AMMONIUM.—$3NH^4S, TeS^2$.—An aqueous solution of tellurite of ammonia, saturated with hydrosulphuric acid gas and evaporated in vacuo over potash, yields pale-yellow, four-sided prisms, which give off hydrosulphate of ammonia when exposed to the air. Even in vacuo, the solution gives off hydrosulphate of ammonia, till the whole space is saturated with its vapour. (Berzelius.)

In Berzelius's *Lehrbuch*, this salt, as well as those which correspond to it, is designated and described as if it contained not $Te S^2$ but TeS^3; this, however, is contrary to the original memoir (*Pogg.* 8, 411), and even to Berzelius's *Lehrbuch* itself (4, 58 and 59).

F. IODOTELLURATE OF AMMONIUM.—A compound of *Biniodide of Tellurium* with *Iodide of Ammonium.*—The solution of biniodide of tellurium in aqueous hydriodic acid, on being saturated with ammonia and left to spontaneous evaporation, yields steel-grey, (often hemitropic) octohedrons and segments of octohedrons, soluble in water and in absolute alcohol. (Berzelius.)

G. CHLOROTELLURITE OF AMMONIUM.—*Protochloride of Tellurium with Chloride of Ammonium.*—Formed by subliming a mixture of sal-ammoniac and a tellurite of a fixed alkali. Ammonia and water [and nitrogen?] are first evolved, and afterwards a black sublimate is formed, having a yellowish radiated fracture, and yielding a greenish-yellow powder. The sublimate, when a very small quantity of water is poured upon it, turns white at first from separation of tellurous acid; this acid then dissolves completely, especially if heat be applied, and leaves metallic tellurium, still exhibiting the radiated texture of the sublimate. A larger quantity of water throws down a mixture of metallic tellurium and tellurous acid, which may be separated by hydrochloric acid: the water holds in solution the following salt, together with free sal-ammoniac. (Berzelius.)

H. CHLOROTELLURATE OF AMMONIUM.—*Bichloride of Tellurium with Chloride of Ammonium.*—The aqueous solution of bichloride of tellurium mixed with sal-ammoniac, yields lemon-yellow, often hemitropic octohedrons and octohedral segments, which dissolve in a small quantity of water without decomposing, and form a colourless liquid, but are decomposed by a larger quantity of water, and by absolute alcohol. (Berzelius.)

TELLURIUM AND POTASSIUM.

A. TELLURIDE OF POTASSIUM.—1. When tellurium conducts the negative electricity of a thousand-pair voltaic battery into hydrate of potash, great heat is evolved, and the tellurium combines with the separated potassium, forming telluride of potassium.—2. Tellurium, heated with potassium in a retort filled with hydrogen gas, combines with the potassium, producing the most vivid combustion.—3. Ten parts of telluric oxide, 2 hydrate of potash, and 1 charcoal, heated in a glass retort to a temperature somewhat below redness, form telluride of potassium, the action being attended with combustion and evolution of carbonic acid.—The alloy obtained by heating telluric oxide containing potash, with charcoal (it contains a smaller quantity of potassium than others), is steel-grey, brittle, and fuses much more easily than pure tellurium. The telluride of potassium obtained by method (1) has the colour of nickel; that obtained by (2) is dark copper-coloured, brittle, has a crystalline fracture, and does not melt below a red heat.

Aqueous Telluride of Potassium or *Hydrotellurate of Potash.*—Telluride of potassium dissolves in water, forming a purple solution; that which is prepared by method (1), and that obtained by fusing the two metals together in equal portions, dissolve without evolution of hydrogen. The solution, when exposed to the air, becomes decolorized, and deposits the whole of the tellurium in thin metal-shining scales; when treated with acids, it evolves hydrotelluric acid gas. (H. Davy.)—Tellurium dissolves in a boiling and highly concentrated solution of potash, forming tellurite and hydrotellurate of potash (or telluride of potassium). But the purple-red solution, both on cooling and on dilution with water, deposits the whole of the tellurium in the form of a grey metallic powder.—Similarly, tellurium-powder heated with dry carbonate of potash, drives out the carbonic acid and forms telluride of potassium and tellurate of potash; but water takes up the caustic alkali, and separates the whole of the tellurium.

B. TELLURITE OF POTASH.—*a. Monotellurite.*—1 At. tellurous acid, fused with an excess of carbonate of potash, drives out 1 At. carbonic acid.—1 At. tellurous acid, slowly heated with 1 At. carbonate of potash, fuses when the heat rises to redness, and on cooling, solidifies in a white mass, consisting of rather large crystals, and exhibiting planes of cleavage. It has an alkaline reaction and caustic taste. Dissolves slowly in cold, more quickly in warm water; the solution evaporated over oil of vitriol in air free from carbonic acid, becomes syrupy, and afterwards solidifies in a granular, non-deliquescent mass. (Berzelius.)

b. Bitellurite.—Formed even by boiling tellurous acid with aqueous solulion of carbonate of potash.—Prepared by heating 2 At. tellurous acid with 1 At. carbonate of potash. The compound fuses somewhat below a red heat, and forms a yellow liquid, which, on cooling, solidifies to a colourless, translucent, distinctly crystalline mass. This mass is resolved by cold water into monotellurite which dissolves, and quadrotellurite which remains undissolved. Boiling water dissolves it completely, but on cooling deposits grains of quadrotellurite; but if it be dissolved in hot water, which already holds in solution a large quantity of the monotellurite, the liquid, when evaporated in the water-bath, deposits the bitellurite in the form of a hard crystalline crust. (Berzelius.)

c. Quadrotellurite.—Formed by boiling fused and pounded tellurous acid for some time with solution of carbonate of potash, filtering at a boiling heat, and leaving the solution to cool. As the liquid cools, the greater part of the salt crystallizes out. The mother-liquid yields an additional quantity on evaporation and cooling. Monotellurite of potash remains in solution.—The quadrotellurite forms pearly grains, which, under the microscope, appear to be formed of regular six-sided prisms and tables.—Cold water decomposes the crystals, extracting monotellurite and bitellurite of potash, and leaving a swollen, gelatinous hydrate of tellurous acid, still retaining the form of the crystals. Boiling water dissolves out bitellurite of potash, and leaves a heavy powder, consisting of anhydrous tellurous acid (which retains, at most, $\frac{1}{3}$ per cent. of the salt); the solution, on cooling, deposits quadrotellurite of potash. The crystals, when heated, give off their water with strong intumescence, and the dehydrated salt fuses at a low red heat, forming a yellow liquid, which, on cooling, yields a transparent and colourless glass. This glass, when pulverized, behaves with boiling water in the same manner as the crystals. (Berzelius.)

	Ignited.		
KO	47·2	....	12·85
$4TeO^2$	320·0	....	87·15
$KO,4TeO^2$	367·2	....	100·00

	Crystallized.				Berzelius.
KO	47·2	....	11·71	....	11·83
$4TeO^2$	320·0	....	79·36	....	79·02
4HO	36·0	....	8·93	....	9·15
+ 4Aq.	403·2	....	100·00	....	100·00

C. TELLURATE OF POTASH.—*a. Monotellurate.*—Formed by boiling 1 At. telluric acid with 1 At. carbonate of potash and with water, till the whole is evaporated to dryness.—2. When crystallized telluric acid in the state of powder, or its concentrated aqueous solution, is supersaturated with caustic potash, monotellurate of potash, which is but slightly soluble in water containing potash, separates from the liquid in the form of a soft, glutinous coagulum: this substance dissolves on the application of a moderate heat, and if the solution be then cooled gradually down to 0°, the salt crystallizes out from it so completely, provided the potash-ley is not too dilute, that the mother-liquid scarcely becomes turbid on the addition of alcohol. The crystals are washed with alcohol. If the potash-ley is weak, the salt does not separate till alcohol is added; if the alcohol be added in moderate quantity and by small portions at a time, the salt separates in oily drops, which are afterwards converted into a mass of crystals; a larger quantity of alcohol causes the salt to separate in crystalline grains.—This salt is likewise formed on heating tellurous acid with nitre to scarcely visible redness, till quadrotellurate of potash is formed, and then adding small portions of bicarbonate of potash as long as effervescence is produced; it is, however, mixed with nitrite and nitrate of potash, and likewise with tellurite of potash, the quantity of the latter increasing with the heat applied to produce the reaction.

Tellurate of potash prepared by method (2) crystallizes in obliquely truncated, three-sided needles united in tufts. The aqueous solution of the salt obtained by the first method yields a crystalline crust, when evaporated in vacuo over oil of vitriol. On evaporating the solution at a moderate heat, the salt remains in the form of a translucent, gummy, fissured mass. The crystals, when heated, give off water and bake together in a white mass. When exposed to the air, they become moist without deliquescing, and are converted into a mixture of bitellurate and carbonate of potash. The salt is soluble in water, but not in alcohol. A small quantity of one of the stronger acids added to the solution, throws down the salt *b*; a quantity just sufficient to give the liquid an alkaline reaction precipitates the salt *c*; a still larger quantity withdraws the whole of the potash, and renders the liquid clear. But if the acid added be the acetic, and the clear mixture be evaporated to dryness and the residue dried at a temperature between 80° and 100°, the telluric acid again takes up the half of the potash, so that a mixture of acetate and bitellurate of potash is ultimately formed. (Berzelius.)

Anhydrous.			*Crystallized.*			Berzelius.
KO	47·2	34·91	KO	47·2	26·19	76·25
TeO^3	88·0	65·09	TeO^3	88·0	48·83	
			5HO	45·0	24·98	23·75
KO,TeO^3	135·2	100·00	+5Aq.	180·2	100·00	100·00

b. Bitellurate.—This salt is formed: 1. When hydrated telluric acid is brought in contact with solution of carbonate of potash.—2. It is, however, produced with greater certainty by dissolving 2 At. hydrated telluric acid and 1 At. carbonate of potash in a small quantity of boiling water, and leaving the solution to cool. As thus obtained, it forms a woolly deposit, which becomes white and earthy on drying; the mother-liquid, when evaporated, yields an additional quantity of salt having a crystalline aspect.—3. The solution of monotellurate of potash exposed to the air in covered vessels deposits bitellurate in hard crystalline grains.—4. By mixing the aqueous solution of the salt *a* with excess of acetic acid, evaporating to dryness, and dissolving out the acetate of potash with alcohol of specific gravity 0·85.—5. By fusing tellurate of potash with nitre till the whole is reduced to a clear liquid; digesting the mass, when cold, in boiling water, to extract the nitrate and nitrite of potash contained in it; and dissolving the residual bitellurate of potash—which is soluble in pure boiling water, but not in water containing nitrate of potash—in a fresh quantity of boiling water: from this solution the salt is deposited on cooling. The higher the temperature at which the mixture is fused, the greater is the quantity of tellurite of potash mixed with the tellurate. This process sometimes yields a modification of the salt, which is insoluble in boiling water or in acids or alkalis, is white when cold, turns yellow when heated, then fuses, gives off oxygen with effervescence, and leaves bitellurite of potash.

The hydrated salt which crystallizes from a hot solution on cooling, is partly woolly, partly granular. On evaporating the aqueous solution over the water-bath, it remains in the form of a white substance, gummy at the edges. It has an alkaline reaction, and a metallic and slightly alkaline taste. When heated, it gives off water, turns yellow, and at a higher temperature, but still below redness, fuses into a mixture of monotellurate and insoluble quadrotellurate of potash; the former may be extracted by water:

$$3(KO,2TeO^3) = 2(KO,TeO^3) + KO,4TeO^3.$$

The bitellurate dissolves sparingly in cold water, much more abundantly in hot water.

	Anhydrous.			*Crystallized.*		*Berzelius.*
KO	47·2	21·15	KO	47·2	18·21	86·1
$2TeO^3$	176·0	78·85	$2TeO^3$	176·0	67·90	
			4HO	36·0	13·89	13·9
$KO,2TeO^3$	223·2	100·00	+4Aq.	259·2	100·00	100·0

c. Quadrotellurate.—α. Containing the soluble modification of Telluric Acid.—1. Crystallizes from a solution of 4 At. telluric acid and 1 At. carbonate of potash in boiling water, in a similar manner to the salt *b*.—2. Falls down on adding nitric acid to an aqueous solution of the monotellurate as long as a precipitate is formed.—3. Tellurous acid is fused with nitre at a heat not higher than commencing redness; the mass dissolved in water; the liquid mixed with a quantity of nitric acid sufficient to give it a slight alkaline reaction, and then left for some hours in contact with the precipitate; and lastly the precipitate is washed on the filter with cold water, care being taken not to use too much.—White, loosely coherent salt. Loses the greater part (7·5 per cent.) of its water at a gentle heat, but retains a small portion (0·15 per cent.) till it turns yellow and is converted into the following salt β: afterwards, when more strongly ignited in the platinum crucible, it gradually gives off 7·71 per cent. of oxygen, and leaves 84·64 per cent. of tellurite of potash. The salt is slightly soluble in water. When it is made to crystallize from its aqueous solution by repeated evaporation and cooling, the crystals are found to be mixed with bitellurate of potash and the mother-liquid contains free telluric acid: if the water likewise contains other salts in solution, this decomposition does not take place. (Berzelius.)

	Anhydrous.			*Crystallized.*		*Berzelius.*
KO	47·2	11·82	KO	47·2	10·84	92·35
$4TeO^3$	352·0	88·18	$4TeO^3$	352·0	80·88	
			4HO	36·0	8·28	7·65
$KO,4TeO^3$	399·2	100·00	+4Aq.	435·2	100·00	100·00

When this salt is prepared by method (1), the solution evaporated to dryness over the water-bath, and the residue treated with water, part of the salt remains behind in the form of a white powder, perfectly insoluble in water but soluble in acids. It has, however, the same composition, but retains the water more tenaciously, and does not part with it till raised to a high temperature, at which it is converted into the following salt. (Berzelius.)

β. Quadrotellurate of Potash containing the insoluble acid.—1. Formed by igniting the soluble quadrotellurate.—2. When tellurous acid is very gently ignited with chlorate of potash (whereupon oxygen and chlorine gases are given off) and the chloride of potassium and chlorate of potash, together with a small portion of bitellurate of potash produced at the same time, are dissolved out by water, the yellow salt β remains behind.—3. Chlorine gas does not act upon cold tellurite of potash; but if the salt be warmed, it absorbs the gas and is converted into a substance of darker colour; and on treating the yellow saline mass with water, after cooling, the yellow salt remains undissolved.—4. The yellow salt is likewise produced on heating the hydrate of telluric acid with chloride of potassium, nitre, and other potash-salts, the heat being kept much below redness. Yellow powder, insoluble at ordinary temperatures in water, and in aqueous sulphuric, nitric, or hydrochloric acid, and also in caustic potash. It dissolves slowly in boiling nitric acid, but more quickly in fused hydrate of potash, the telluric acid then passing from the insoluble to the soluble state. Anhydrous telluric acid boiled with moderately concentrated solution of potash, does not dissolve but takes up a small quantity of the alkali. (Berzelius.)

D. SULPHOTELLURITE OF POTASSIUM.—Separates from a dilute solution evaporated in vacuo or from a concentrated solution evaporated in the air at 40°, in pale-yellow, four-sided prisms, easily melting to a black liquid, which, on cooling, solidifies to a brownish-yellow mass, soluble again in water. In damp air, it becomes moist and soon blackens from decomposition; the dilute solution likewise decomposes quickly in the air. (Berzelius.)

E. IODOTELLURATE OF POTASSIUM. — *Biniodide of Tellurium with Iodide of Potassium.*—Formed when a solution of biniodide of tellurium in concentrated hydriodic acid is exactly saturated with potash, or mixed with iodide of potassium, and left to evaporate spontaneously. Steel-grey prisms and rhombic tables having a strong metallic lustre; they are easily soluble in water, and form a brown solution, which, when a large quantity of water is added to it, becomes turbid and yields a slight precipitate. (Berzelius.)

F. BROMOTELLURATE OF POTASSIUM.—*Bibromide of Tellurium with Bromide of Potassium.* — Formed by mixing an aqueous solution of bibromide of tellurium with chloride of potassium, and setting the liquid aside to crystallize. Bichloride and bibromide of tellurium remain in the solution. Cinnabar-red, short rhombic prisms or large rhombic tables, frequently hemitropic with a re-entering angle. Permanent in the air. Decomposed by a large quantity of water and likewise by alcohol. (Berzelius.)

G. CHLOROTELLURATE OF POTASSIUM.—*Bichloride of Tellurium with Chloride of Potassium.*—Formed by dissolving chloride of potassium in a solution of tellurous acid in hydrochloric acid, and leaving the liquid to evaporate spontaneously. Colourless chloride of potassium crystallizes out first: afterwards, when the liquid is reduced to a syrupy consistence, the double salt separates: it must be dried between folds of bibulous paper. Lemon-yellow crystals which are permanent in a dry winter atmosphere, but deliquesce in the air in its ordinary state; they are decomposible by water and by absolute alcohol. (Berzelius.)

TELLURIUM AND SODIUM.

A. TELLURIDE OF SODIUM.—Behaves like telluride of potassium.

B. TELLURITE OF SODA.—*a. Monotellurite.*—1 At. tellurous acid heated with 1 At. carbonate of soda fuses at a full red heat, and forms a mass, which, as it cools, but while still red hot, solidifies in large regular crystals; if it be rapidly cooled, it swells up in vegetations. Dissolves slowly but completely in cold water, and more quickly in warm water, from which it does not separate on cooling. Alcohol throws down from the solution a concentrated liquid, which, after a few days, yields large crystals of the hydrated salt. The solution evaporated in vacuo over oil of vitriol, leaves a white earthy mass. (Berzelius.)

b. Bitellurite.—Formed by fusing 2 At. tellurous acid with 1 At. carbonate of soda. Fuses readily and crystallizes on cooling, but less distinctly than the salt *a*. Decomposed by water in the same manner as the potash-salt. (Berzelius.)

c. Quadrotellurite.—Separates from the boiling hot aqueous solution of the salt *b*, on slow cooling, in pearly scales and thin six-sided tables. Behaves like the potash-salt, but swells up more strongly when heated, and yields a transparent and colourless glass. (Berzelius.)

	Anhydrous.			*Crystallized.*		Berzelius.
NaO	31·2	8·88	NaO	31·2	7·88	8·32
$4TeO^2$	320·0	91·12	$4TeO^2$	320·0	80·77	80·46
			5HO	45·0	11·35	11·22
$NaO,4TeO^2$	351·2	100·00	+ 5Aq.	396·2	100·00	100·00

Before the blowpipe, tellurous acid forms with carbonate of soda on platinum, a transparent and colourless glass, which becomes white on cooling, and is easily reduced on charcoal. (Berzelius.)

C. TELLURATE OF SODA.—Tellurous acid behaves with nitrate of soda when fused with it, in the same manner as with nitrate of potash (pp. 417....419).—*a. Monotellurate.*—The hydrated salt separates from the solution of hydrated telluric acid in excess of warm soda-ley, partly on cooling, partly on the addition of alcohol, either in grains or in the form of a crystalline crust. It is also obtained by dissolving 1 At. hydrated telluric acid and 1 At. carbonate of soda in water, and evaporating to complete dryness at a temperature below 100°: it is only by evaporating to dryness that the carbonic acid can be completely driven out. The crystals do not part with all their water till they are heated nearly to redness. They are but sparingly soluble either in cold or in hot water: from the latter solution they do not separate on cooling. On adding an excess of soda, however, the salt is deposited in grains. The aqueous solution evaporated over the water-bath leaves at first a soft, gummy mass easily soluble in water, but after complete drying it again leaves a difficultly soluble compound. (Berzelius.) The salt dehydrated by heating to a temperature short of redness, remains white even when hot, and dissolves in heated dilute nitric acid, but not in water either hot or cold, in which on the contrary it diffuses itself and produces milkiness.

	Anhydrous.			*Crystallized.*		Berzelius.
NaO	31·2	26·18	NaO	31·2	22·74	86·9
TeO^2	88·0	73·82	TeO^2	88·0	64·14	
			2HO	18·0	13·12	13·1
NaO,TeO^2	119·2	100·00	+ 2Aq.	137·2	100·00	100·0

b. Bitellurate.—1. Prepared by dissolving hydrate of telluric acid in boiling carbonate of soda, and adding acetic acid after cooling,—whereupon the bitellurate, which is at first precipitated, is decomposed by the excess of acetic acid and redissolved. The clear mixture, on being evaporated to dryness and heated till no more acetic acid is given off, leaves a mixture of acetate and bitellurate of soda, the first of which may be extracted by alcohol. The bitellurate of soda remains in the form of a white powder, containing 14 per cent. (4 At.) of water, and slowly but completely soluble in water. The solution, when left to spontaneous evaporation, dries up to a fissured gummy mass, which, when heated, becomes milk-white and detaches itself from the glass; it dissolves completely, though very slowly, in water. The salt, when heated till deprived of its water, is converted into a yellow mixture of quadrotellurate and monotellurate of soda, the former of which is insoluble, while the latter may be extracted by continued washing with water. The same salt is obtained by dissolving 2 At. hydrated telluric acid and 1 At. carbonate of soda in water. If an additional atom of carbonate of soda be added to this solution, no monotellurate of soda is formed—but, on evaporating the liquid at a gentle heat, clear, syrupy drops of the bitellurate are deposited, and the supernatant liquid is found to contain carbonate of soda. (Berzelius.)

c. Quadrotellurate.—α. Containing the soluble acid.—An aqueous solution of 4 At. hydrated telluric acid and 1 At. carbonate of soda leaves, when spontaneously evaporated, a clear, somewhat fissured, but still soft gum, which, when gently heated, dries up to a milk-white mass adhering firmly to the glass vessel. This mass dissolves slowly in cold water, leaving a white powder; and if the solution be evaporated to dryness, the residue when treated with cold water again leaves a white powder, and so on.

This white powder contains the same quantity of water as the soluble salt, but, like the corresponding modification of the potash-salt, it is insoluble even in boiling water. (Berzelius.)

β. Containing the insoluble acid.—Both the soluble quadrotellurate and the white powder obtained by gently heating it, are converted by a stronger heat into the anhydrous, yellow, insoluble salt. (Berzelius.)

D. With *Borax* or *Microcosmic salt,* tellurous acid yields on platinum a transparent and colourless glass which, when heated on charcoal, becomes grey and turbid from reduction of tellurium. (Berzelius.)

E. SULPHOTELLURITE OF SODIUM.—$3NaS,TeS^2$.—Formed by saturating an aqueous solution of tellurite of soda with hydrosulphuric acid gas, filtering from the precipitated sulphide of tellurium, and evaporating the filtrate in vacuo. There remains a non-crystalline, pale-yellow mass, which is easily decomposed by exposure to the air, and, when analysed by hydrochloric acid, yields 40·5 parts of chloride of sodium for every 22 parts of bisulphide of tellurium. (Berzelius.)

F. IODOTELLURATE OF SODIUM.—Crystallizes with difficulty from the aqueous solution on evaporation. The crystals are brown without metallic lustre; contain water of crystallization; deliquesce in moist air, and are very easily soluble in water and alcohol. (Berzelius.)

G. FLUO-TELLURATE OF SODIUM.—*Bifluoride of Tellurium with Fluoride of Sodium.*—Ill-defined crystals, decomposible by cold water, soluble in a very small quantity of boiling water. (Berzelius.)

TELLURIUM AND LITHIUM.

A. TELLURITE OF LITHIA.—*a. Monotellurite.*—The mass obtained by fusing tellurous acid with carbonate of lithia in equivalent proportions, crystallizes when slowly cooled, but swells up like the soda-salt if cooled rapidly. The aqueous solution placed over oil of vitriol dries up to a white, earthy, scarcely crystalline mass. (Berzelius.)—*b. Bitellurite.*—Easily fusible; crystallizes on cooling. Decomposed by cold water into monotellurate and quadrotellurate. Dissolves in boiling water, which, however, likewise deposits the quadrotellurite.—*c. Quadrotellurite.*—Milk-white grains; behaves like the corresponding potash and soda salts when fused or when treated with water. (Berzelius.)

B. TELLURATE OF LITHIA.—*a.* and *b.* *Monotellurate* and *Bitellurate.*—The aqueous solution of either of these salts yields, on evaporation, a transparent gum, which, when perfectly dried by heat, becomes milk-white and sticks to the glass.—*c.* *Quadrotellurate.*—Exhibits precisely similar characters. If heated to 100° after drying, it yields a white, insoluble powder, similar to that produced from the potash and soda salts, and, at a stronger heat, gives off water, and is converted into the yellow compound. (Berzelius.)

C. SULPHOTELLURITE OF LITHIUM.—The solution dries up in vacuo to a pale yellow, amorphous, saline mass, which decomposes very easily when exposed to the air. (Berzelius.)

TELLURIUM AND BARIUM.

A. TELLURITE OF BARYTA.—*a.* *Monotellurite.*—1. When 1 At. tellurous acid is heated to redness with 1 At. carbonate of baryta, the whole of the carbonic acid is driven off, and a yellow liquid formed, which, on cooling, solidifies in a mass of colourless crystals.—2. By double decomposition, hydrated, white, voluminous flakes are obtained. Both the anhydrous and the hydrated salt are but very slightly soluble in water. The solution has an alkaline reaction, and, when exposed to the air, deposits carbonate and quadrotellurite of baryta. (Berzelius.)

b. *Quadrotellurite.*—1. When 4 At. tellurous acid and 1 At. carbonate of baryta are heated together to low redness, the mixture fuses, and yields a transparent and colourless glass on cooling.—2. Very weak nitric acid added to the aqueous solution of monotellurite of baryta throws down very bulky flakes. These flakes dissolve when acted upon by warm nitric acid in excess; the solution, when evaporated, deposits no tellurous acid till the nitric acid begins to evaporate. (Berzelius.)

B. TELLURATE OF BARYTA.—*a.* *Monotellurate.*—Formed by precipitating the aqueous solution of chloride of barium with monotellurate of soda. The precipitate, which is bulky at first, soon sinks down in the form of a heavy white powder. If bitellurate is likewise present, this effect does not take place, except on the addition of ammonia. The precipitate, after washing and drying, forms a white mealy powder. This powder when heated above 200° gives off its water before the acid begins to decompose. It is slightly soluble in cold water, but more soluble in boiling water, on the evaporation of which, it remains in the form of a white earth. Dissolves easily and without decomposition in nitric acid; not decomposed by ammonia. (Berzelius.)

	Anhydrous.			*Hydrated.*		*Berzelius.*
BaO	76·6	46·54	BaO	76·6	39·98	39·82
TeO^3	88·0	53·46	TeO^3	88·0	45·93	45·85
			3HO	27·0	14·09	14·33
BaO,TeO^3	164·6	100·00	+ 3Aq.	191·6	100·00	100·00

b. *Bitellurate.*—Aqueous bitellurate of soda added to solution of chloride of barium throws down white voluminous flakes which do not agglomerate. They contain 10 per cent. (3 At.) of water. Water extracts from them a salt containing a larger quantity of acid, and leaves the salt *a* undissolved. (Berzelius.)

c. Quadrotellurate.—Formed by precipitating a baryta-salt with quadrotellurate of soda. Bulky, and more easily soluble in water than *a* or *b*. Turns yellow when heated, but recovers its whiteness on cooling. When dissolved in acetic acid and evaporated, it remains in the form of a white earthy mass. (Berzelius.)

C. SULPHOTELLURITE OF BARIUM.—Formed by boiling sulphide of barium with bisulphide of tellurium and water, and evaporating the filtrate in vacuo. Large, transparent, pale-yellow, flat, obliquely truncated, four-sided prisms, which are tolerably permanent in the air, and dissolve very slowly in water. (Berzelius.)

TELLURIUM AND STRONTIUM.

A. TELLURITE OF STRONTIA.—As with baryta.

B. TELLURATE OF STRONTIA.—*Monotellurate.*—Formed by double affinity. White flakes, which do not agglomerate; soluble in a large quantity of water. (Berzelius.)

C. SULPHOTELLURITE OF STRONTIUM.—Formed by boiling sulphide of strontium with water and bisulphide of tellurium. The filtrate evaporated in vacuo to the consistence of a syrup, shows signs of crystallization and dries up to a pale-yellow mass, tolerably permanent in the air, and perfectly soluble in water.

TELLURIUM AND CALCIUM.

A. TELLURITE OF LIME.—*a. Monotellurite.*—1. On igniting 4 At. tellurous acid with 1 At. lime, a white saline mass is obtained, which does not fuse at the melting point of silver.—2. By double decomposition:—White flakes, slightly soluble in cold water, more soluble in hot water. When the water is evaporated, the salt remains in the form of a white earth. (Berzelius.)—*b. Bitellurite.*—Fuses when heated nearly to whiteness, and on cooling, solidifies in an opaque cake, which, when gently pressed, is found to be made up of micaceous scales. (Berzelius.)—*c. Quadrotellurite.*—Fuses somewhat more readily than *b*, giving off vapours of tellurous acid, and likewise solidifies in micaceous scales on cooling.

B. TELLURATE OF LIME.—*Monotellurate.*—By double decomposition. White flakes which do not agglomerate. The solution in hot water leaves the salt, on evaporation, in the form of a white powder. (Berzelius.)

C. SULPHOTELLURITE OF CALCIUM.—Yellow, non-crystalline, soluble mass, which decomposes rapidly when exposed to the air. (Berzelius.)

TELLURIUM AND MAGNESIUM.

A. TELLURITE OF MAGNESIA.—Formed by mixing concentrated solutions of monotellurite of soda and a magnesia-salt. Much more soluble than the baryta, strontia, or lime-salt. The solution, when exposed to the air, deposits a mixture of carbonate and *Quadrotellurite of Magnesia* in white flakes.

B. TELLURATE OF MAGNESIA.—*a. Monotellurate.*—Formed by mixing concentrated solutions of monotellurate of soda and a magnesia-salt. White flakes, more soluble in water than the corresponding salts of the earthy alkalis.—*b. Bitellurate.*—By double decomposition with a concentrated solution of bitellurate of soda. Still more soluble in water.

C. SULPHOTELLURITE OF MAGNESIUM.—By precipitating the barium compound with sulphate of magnesia, and evaporating the filtrate in vacuo. Pale-yellow, crystalline, saline mass, soluble in water, and with tolerable facility in alcohol. (Berzelius.)

TELLURIUM AND CERIUM.

SULPHOTELLURITE OF CERIUM.—By precipitating an aqueous solution of a cerous salt with sulphotellurite of potassium. The precipitate, which is brownish-yellow at first, soon acquires the dark colour of bisulphide of tellurium; after drying, it evolves sulphur on distillation. (Berzelius.)

TELLURIUM AND YTTRIUM.

A. TELLURITE OF YTTRIA.—By double decomposition. White, voluminous flakes, insoluble in excess of the yttria-salt.

B. TELLURATE OF YTTRIA.—Yttria-salts give with mono- and bitellurate of soda, white flakes, insoluble in water and in excess of the yttria-salt. (Berzelius.)

TELLURIUM AND GLUCINUM.

A. TELLURIDE OF GLUCINUM.—The two metals, when heated together, unite without ignition, and form a white powder, which smells of hydrotelluric acid on exposure to the air, and when thrown into water, evolves that gas with violence. (Wöhler.)

B. and C. TELLURITE AND TELLURATE OF GLUCINA.—Similar to the corresponding yttria-salts. (Berzelius.)

TELLURIUM AND ALUMINUM.

A. TELLURIDE OF ALUMINUM.—When a mixture of pounded tellurium and aluminum is heated, combination takes place, attended with such violent combustion, that the mass is projected from the tube like a shot; for this reason, the tellurium must be added in small pieces. Black, metallic-shining, sintered, brittle mass, which exhales an intolerable smell of telluretted hydrogen when exposed to the air, and evolves that gas with violence when immersed in water, the water quickly becoming red, and afterwards brown and opaque, from separation of tellurium. (Wöhler, *Pogg.* 11, 161.)

B. TELLURITE OF ALUMINA.—By double decomposition. White flakes, insoluble in excess of the alumina-salt.

C. TELLURATE OF ALUMINA.—By double decomposition. White flakes, soluble in excess of the alumina-salt. (Berzelius.)

TELLURIUM AND THORINUM.

TELLURITE AND TELLURATE OF THORINA.—By double decomposition. White precipitate, insoluble in excess of the thorina-salt. (Berzelius.)

TELLURIUM AND ZIRCONIUM.

A. TELLURITE OF ZIRCONIA.—By double decomposition. White flakes.

B. TELLURITE OF ZIRCONIA.—Formed by precipitating monohydrochlorate of zirconia with monotellurate of soda. Voluminous, semi-transparent precipitate, soluble in excess of hydrochlorate of zirconia. (Berzelius.)

TELLURIUM AND CHROMIUM.

A. TELLURITE OF CHROMIC OXIDE.—By double decomposition. Pale greenish-grey, bulky precipitate, soluble in excess of the chromic salt.

B. TELLURATE OF CHROMIC OXIDE.—Greyish-green flakes, reddish by transmitted light, soluble in excess of the chromic-salt. (Berzelius.)

TELLURIUM AND URANIUM.

A. TELLURITE OF URANIC OXIDE.—Pale lemon-coloured insoluble salt.

B. TELLURATE OF URANIC OXIDE.—Bulky, pale-yellow salt, insoluble in excess of uranic nitrate. (Berzelius.)

TELLURIUM AND MANGANESE.

TELLURITE AND TELLURATE OF MANGANOUS OXIDE.—White flakes, which, after uniting into a mass, exhibit a reddish tint. (Berzelius.)

With sulphotellurite of potassium, manganous salts behave like cerous salts. (Berzelius.)

OTHER COMPOUNDS OF TELLURIUM.

With Bismuth, Zinc, Tin, Lead, Iron, Copper, Mercury, Silver, and Gold, both in artificial and in natural compounds.

Chapter XXVII.

BISMUTH.

Berzelius. *Gilb.* 40, 286. Further: *Schw.* 7, 70.
Lagerhjelm. *Schw.* 17, 416.
Jacquelain. *Ann. Chim. Phys.* 66, 113; also *J. pr. Chem.* 14, 1.
A. Stromeyer. *Pogg.* 26, 549.
Heintz. *Pogg.* 63, 55; abstr. *Ann. Pharm.* 52, 252.
Arppe. *Pogg.* 64, 237; abstr. *Ann. Pharm.* 56, 237.
Gladstone. *Chem. Soc. Mem.* 3, 480; abstr. *Liebig and Kopp's Jahresbericht*, 1, 432 (1847–8.)

Synonymes.—*Wismuth, Bismuthum, Marcasita.*

History. Recognized as a distinct metal by Agricola in 1529; more fully examined by Pott, Geoffroy, Berzelius, Lagerhjelm, J. Davy, and Jacquelain. The existence of bismuthic acid was established by Bucholz & Brandes (*Schw.* 22, 33), and by A. Stromeyer, Jacquelain, and Fremy.

Sources. Not very abundant; mostly native; also as oxide; as carbonate; as sulphide, either alone or in combination with other metallic sulphides, as in Nickeliferous bismuth-glance, Needle-ore, and Bismuth-lead-ore; also as Telluric bismuth.

Preparation on the large scale.—Native bismuth is separated from the matrix by fusion at a gentle heat.

Purification. Commercial bismuth, which may contain arsenic, iron, nickel, copper, and other metals, is dissolved in nitric acid; the clear solution poured off and precipitated by water, and the precipitated mononitrate of bismuth reduced at a moderate heat, either in a charcoal crucible or with black flux. Arsenical bismuth, fused with twice its weight of zinc, forms an alloy which yields arseniuretted hydrogen in Marsh's apparatus (p. 269). *Reinsch.*

Properties. Crystallizes in octohedrons and cubes, exhibiting very distinct cleavage-planes parallel to the lateral faces of the octohedron. Bismuth may be obtained in beautiful crystals by melting the ordinary metal of commerce in a crucible, adding nitre from time to time, and stirring, till—after the metal has been kept for some hours at a temperature as high as the melting point of nitre—a portion of the fused metal taken out and exposed to the air, no longer assumes an indigo-blue and afterwards a violet or rose colour which disappears on cooling, but a fine green or golden-yellow tint, and retains it after cooling. The bismuth is then immediately poured into a heated pot, which is then covered with a hot muffle to prevent the surface from solidifying before the other part; the whole cooled pretty quickly (if the cooling be too slow, the metal deposits itself in layers, not in fine crystals); the crust formed on the surface pierced with a hot coal, as soon as the mass is half solidified, and the portion which still remains liquid poured out. (Quesneville, *J. Pharm.* 16, 554; also *Schw.* 60, 378.)

Specific gravity of purified bismuth: 9·6542 (Karsten); 9·799 at 19° (Marchand & Scheerer); of commercial bismuth: 9·822 (Brisson); 9·833 (Herapath); 9·861 (Bergman). Strong pressure rather diminishes than increases the density. If commercial bismuth, of specific gravity 9·783, be formed into a cylinder of such a size as to go into a steel diamond mortar, and subjected to very strong pressure, it is found that, under a pressure of 100,000 pounds, the metal retains its crystalline texture and tenacity, and has a density of 9·779; a pressure of 150,000 pounds reduces the density to 9·655; under 200,000 pounds' pressure—which causes the steel to crack—the bismuth becomes very brittle, appears like grey steel on the fractured surface, exhibits scarcely any crystalline structure under the microscope, and has a density of only 9·556 (Marchand & Scheerer, *J. pr. Chem.* 27, 209.) Moderately hard, slightly sonorous; brittle, but may be somewhat extended by careful hammering. Reddish tin-white, with moderate lustre. Fuses at 249° (Crighton); at 264° (Rudberg); 265° (G. Herman, *Pogg.* 20, 283), and if cooled from that temperature, solidifies with an expansion of at least $\frac{1}{32}$ (I., 256.) Boils at a dull white heat, and if air be excluded, sublimes in laminæ.

Atomic weight of Bismuth.—The atomic weight of bismuth is 71, or $1\frac{1}{2} . 71 = 106{\cdot}5$, or $3 . 71 = 213$, accordingly as bismuth-oxide is regarded as BiO, or as Bi^2O^3, or as BiO^3. The similarity of bismuth to antimony renders the last supposition the most probable of the three. According to the author's experiments, the number 213 ought to be reduced to 210, or even lower.

Compounds of Bismuth.

BISMUTH AND OXYGEN.

A. *Suboxide of Bismuth?*

The metal, when exposed to the air at ordinary temperatures, becomes covered with a thin film of this substance; when heated in the air till it fuses, it likewise becomes covered with this film, which is renewed as often as it is removed, until the whole of the metal is converted into suboxide: *Bismuth-ash.*—Brownish or dark purple-brown. When treated with hydrochloric acid, it is resolved into teroxide and metallic bismuth. By heating *magistery of bismuth* with protochloride of tin, a black powder is produced, which, after washing and drying, glimmers, when heated, with a yellowish-green light, and is converted into teroxide of bismuth; it turns yellow in the air at ordinary temperatures, and is soluble in heated hydrochloric acid. (A. Vogel, *Kastn. Arch.* 23, 86.) When bismuth is heated with microcosmic salt on charcoal in the inner blowpipe flame, a clear glass is obtained, which turns black on cooling. (Berzelius.)—Berzelius regards this substance as a peculiar oxide, but Proust and Sir H. Davy regard it as a mixture of metal and oxide.

¶ If a plate of pure bismuth be immersed in a solution of 1 part of caustic potash in 5 or 6 parts of water, and made to form the positive pole of a two-pair Grove's battery, the negative pole being formed of platinum, the bismuth becomes successively yellow, red, violet, blue, green, and then again colourless, after which the same series of colours is reproduced, but less strongly. By interrupting the current at the proper time, any colour of the series may be fixed. (Poggendorff, *Pogg.* 74, 586.) ¶

B. BISMUTH-OXIDE.* BiO^3.

Teroxide of Bismuth, Wismuthoxyd, Oxide bismuthique.—Found in an impure state, as *Bismuth-ochre.*

Formation.—1. The metal, when heated in the air till it boils, burns with a faint bluish-white flame, and the vapours of the resulting bismuth-oxide condense on colder bodies: *Flowers of Bismuth, Flores Bismuthi.*—2. When bismuth is melted in the air for a long time, and the surface frequently renewed, it is at first converted into suboxide of bismuth, which, by longer heating in the air, is transformed into the teroxide.—3. Bismuth does not oxidize in moist air at ordinary temperatures; but if it is partially covered with water, and the air, at the same time, is freed from carbonic acid, the hydrated oxide is formed at first, and afterwards a small quantity of yellow oxide in delicate crystals; but if the air is not freed from carbonic acid, hydrated carbonate of the oxide is immediately formed in white scales, and the surface of the metal becomes tarnished, first with a red-brown, and then with a blue film. (Bonsdorff, *Pogg.* 41, 305.)—4. Bismuth at a white heat decomposes vapour of water, and forms the teroxide. (Regnault.) It does not evolve hydrogen with boiling concentrated hydrochloric acid.—5. Bismuth decomposes nitric acid at ordinary temperatures, and oil of vitriol when heated, nitric oxide or sulphurous being evolved and a bismuth-salt produced. Fuming nitric acid produces deflagration with melted bismuth (Proust), and heats bismuth-powder to redness. (Berzelius.)

Preparation.—1. By gently heating bismuth in the air, and stirring constantly.—2. By gently igniting the mononitrate or the carbonate.—3. By fusing the hydrated oxide in excess with caustic potash (Jacquelain), or by boiling the hydrated oxide with caustic potash or soda, the anhydrous oxide is obtained in the crystalline state.

Properties.—Prepared by (1) or (2): Pale lemon-yellow powder, which, when heated, assumes for a while an orange-yellow, and afterwards a red-brown tint; by (3): yellow, shining needles. Specific gravity of

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[*] For oxides which form salifiable bases, it is important to have names as short as possible, and so constructed as easily to enter into compound names. For this reason, the term *Bismuth-oxide* is preferable to *oxide of bismuth.* Such names as *sulphate of bismuth-oxide* are convenient enough, whereas terms like *Sulphate of oxide of bismuth* are intolerably awkward and prolix. The still shorter terms *Bismuth-sulphate, Bismuth-nitrate,* &c., are also convenient in many cases, and perfectly definite. When a metal forms two classes of salts (*e. g.*, iron and copper) it is necessary to distinguish these salts and the corresponding oxides by the terminations *ous* and *ic*, a method which has already been adopted in several instances in the course of this work (*vid.* Cerium, Uranium, Chromium, &c.); but for metals which form but one class of salts, (*e. g.*, bismuth, zinc, lead, silver) these terminations are superfluous. [W.]

the oxide obtained from the mononitrate: 8·1735 (Karsten), 8·968 (Pol. Boullay). Fuses at a strong red heat, and solidifies on cooling—provided that an earthen crucible has not been used—in a crystalline mass. (Fuchs, *Schw.* 67, 429.) If the oxide is fused in an earthen crucible, silica becomes mixed with it, and the dark brown liquid solidifies to a yellowish, opaque glass, whose density at 4° in vacuo, according to Le Royer & Dumas, is 8·449. The oxide volatilizes only at very high temperatures.

			J. Davy, Thomson.	Lager-hjelm.	Gmelin.	Klaproth, Bucholz.	Proust.	Mor-veau.
Bi	213	89·87	90	89·863	89·67	89·28	88	80
3O	24	10·13	10	10·137	10·33	10·72	12	20
BiO^3	237	100·00	100	100·000	100·00	100·00	100	100

Decompositions.—By gently heated potassium or sodium the oxide is reduced to the metallic state, with slight ignition (Gay-Lussac & Thénard); by charcoal—easily before the blowpipe—to the metallic state; by carbonic oxide to the metallic state. (Gm.) By sulphur it is converted into sulphide.

Combinations.—*a.* With Water.—HYDRATE OF BISMUTH-OXIDE.—Precipitated, on mixing the aqueous solution of the nitrate with an alkali, in white flakes which dry up to a white powder. If the hydrochlorate is used instead of the nitrate, the precipitate contains chloride of bismuth mixed with the hydrated oxide. (A. Stromeyer.)

b. With acids, forming the SALTS OF BISMUTH-OXIDE, or BISMUTH-SALTS.—Bismuth-oxide dissolves easily in aqueous acids. Some of the salts are obtained by treating the metal with an oxidating acid. Bismuth-salts are very heavy; they are colourless, unless the acid itself is coloured; they exert a poisonous action. Those which contain a volatile acid part with it on ignition. When fused on charcoal before the blowpipe, they yield a button of bismuth and produce a yellow deposit on the charcoal. Zinc, tin, cadmium, lead, iron, and copper precipitate the bismuth from their solutions in the metallic state. Zinc, cadmium, tin, and iron reduce the bismuth quickly and completely, the two former with rapid evolution of gas and great rise of temperature, the two latter quietly. After the free acid of the bismuth salt has been saturated, a basic salt of bismuth is precipitated, and this is likewise reduced, but very slowly. The reduced bismuth presents the appearance of a blackish-grey dendritic powder, destitute of metallic lustre. The reducing action of the lead ceases after a time. Copper, antimony, and arsenic have no action on bismuth-salts. (Fischer, *Pogg.* 8, 497.) Copper precipitates the bismuth very slowly and imperfectly. (Jacquelain.) In a solution of mononitrate of bismuth in 500 parts of dilute hydrochloric acid, the copper immediately becomes covered with a grey metallic film, which gradually accumulates in the form of small laminated crystals. On the application of heat, the whole of the bismuth is deposited on the copper in the form of a crystalline film. Reduction likewise takes place even with solutions still more dilute. (Reinsch, *J. pr. Chem.* 24, 248.) Water decomposes most bismuth-salts—provided they do not contain too large an excess of acid—into dilute acid containing a small quantity of oxide in solution, and an insoluble or difficultly soluble basic salt. Caustic ammonia, potash, soda, and baryta generally precipitate the white hydrate (from the hydrochlorate, however, they throw down a basic salt), and on boiling, especially if they are concentrated, they precipitate the yellow anhydrous oxide. (A. Stromeyer, *Pogg.* 26, 553; Jacquelain); the precipitate is insoluble in excess of alkali, even on boiling. (Stromeyer.) Alkaline carbonates throw down white carbonate of bismuth-oxide, somewhat soluble in excess, but precipitable from the solution by a caustic alkali. (A. Stromeyer.) According to L. Laugier (*Ann. Chim. Phys.* 36, 332), the precipitate is perfectly soluble in excess of carbonate of ammonia, slightly soluble in carbonate of potash, but perfectly insoluble in carbonate of soda; according to Berzelius, however (*Jahresber.* 12, 166), bismuth-oxide is not soluble in excess of carbonate of ammonia, unless phosphoric or arsenic acid is present. Carbonate of lime added to a solution of the nitrate completely precipitates the hydrated oxide, even in the cold (Liebig, *Mag. Pharm.* 35, 114); so likewise do the carbonates of baryta, strontia, and magnesia. (Demarçay, *Ann. Pharm.* 11, 240.) Phosphate of soda precipitates white phosphate of bismuth-oxide. Hydrosulphuric acid throws down all the bismuth in the form of brown-black sulphide, even when a large excess of acid is present; so likewise do the alkaline hydrosulphates, the precipitate not being soluble in excess. Iodide of potassium throws down brown iodide of bismuth, easily soluble in excess of the iodide. Alkaline chromates precipitate lemon-yellow chromate of bismuth-oxide. Oxalic acid gives, after a while, a crystalline precipitate of oxalate of bismuth-oxide. Infusion of galls gives a brownish-yellow precipitate. Ferrocyanide of potassium produces a white precipitate soluble in hydrochloric acid; ferricyanide of potassium, a pale yellow precipitate soluble in hydrochloric acid. Sulphuric acid, and hyposulphite of soda with addition of hydrochloric acid, do not precipitate bismuth.

c. With Silicic acid, with Glass-fluxes, and with several heavy metallic oxides, forming vitreous masses.

¶ C. Peroxide of Bismuth. BiO^4.

When the yellow hydrate of bismuth-oxide is boiled with an alkaline chlorite having a strong alkaline reaction, it turns brown, like peroxide of lead, and is converted into the peroxide. (Arppe.) According to Heintz, this compound is likewise formed by treating the teroxide with strong caustic potash and chlorine; but, according to Stromeyer and Arppe, this process yields bismuthic acid, BiO^5 (*vid.* p. 432).

	Calculation.			Arppe.		
Bi	213	86·93		86·52	86·70	85·93
4O	32	13·07		13·11	13·05	13·32
Water				0·37	0·25	0·75
	245	100·00		100·00	100·00	100·00

By boiling with nitric acid, the peroxide is perfectly dissolved; any yellow or green residue that may be left behind proceeds from an admixture of bismuthic acid. (Arppe.)

Hydrated Peroxide.—When a bismuth-salt contains free chlorine, caustic potash produces in it, not a white but a yellow precipitate, which consists of the hydrate of a higher oxide, but can never be obtained free from chlorine. When boiled with potash, it gives off water and is converted into a light brown substance, containing bismuth 88·04....88·15, oxygen 11·79....11·62, water 0·27....0·23, which nearly corresponds to the formula: $3BiO^3 + BiO^5 = Bi^4O^{14}$. ¶

BISMUTHIC ACID. BiO^5 ?

Wismuthsäure, Acide Bismuthique, Peroxide of Bismuth.

When teroxide of bismuth is ignited with excess of potash- or soda-hydrate, and the air has access to the mixture—and likewise when chlorine acts upon the teroxide diffused through caustic potash,—a double salt is formed consisting of bismuthate of bismuth-oxide and the alkali. ¶ According to Arppe, this latter process yields a hydrate of bismuthic acid, if the alkali is used in very large excess, and the anhydrous acid if the quantity of alkali is somewhat less. ¶

Preparation.—1. By treating brown bismuthate of bismuth-oxide and potash (p. 445) with a cold mixture of 1 part of nitric acid and 9 parts water, then with a more dilute acid, and afterwards washing with water and drying. (A. Stromeyer, *Pogg.* 26, 549; Brandes, *Schw.* 69, 158.)—2. By fusing bismuth-oxide with hydrate of soda, boiling the mass with excess of soda-ley, and washing the brown powder which separates, first with nitric acid, and then with water. (Fremy, *Compt. rend.* 15, 1108; also *N. J. Pharm.* 3, 30; see also Arppe, *Ann. Pharm.* 56, 239.)

	Calculation.			Arppe.
Bi ..	213	....	84·19	84·26
5O ..	40	....	15·81	15·74
BiO^5	253		100·00	100·00

Or:	Calculation.				Stromeyer.		Brande
BiO^3	237	....	93·68	....	95·14	....	95
2O	16	....	6·32	....	4·86	....	5
BiO^5	253	....	100·00		100·00		100

Jacquelain regards bismuthic acid as BiO^4: A. Stromeyer, from his analysis, assigns to bismuthic acid 1½ times as much oxygen as to bismuth-oxide. The difficulty of obtaining bismuthic acid free from bismuth-oxide renders it probable that the oxygen in the former has been estimated too low rather than too high, and consequently that pure bismuthic acid is really BiO^5, corresponding to antimonic acid.

Decompositions.—At the temperature of boiling mercury, bismuthic acid is resolved into oxygen gas and the yellow oxide, without giving off water. When a mixture of this acid with charcoal, sugar, or other organic substances is set on fire by a red-hot coal, it burns slowly away like tinder, without deflagration. Hydrogen gas reduces the acid to the state of oxide at a temperature below that at which the acid gives off oxygen when heated alone; at a red heat, hydrogen reduces it to the metallic state. Sulphurous acid, in the state of aqueous solution—but not in the gaseous form,—slowly converts the acid into sulphate of bismuth-oxide. Oil of vitriol instantly disengages oxygen gas from it, dilute sulphuric acid more slowly. Phosphoric acid acts in the same manner. Cold nitric acid does not dissolve bismuthic acid, unless it contains nitrous acid; heated nitric acid disengages oxygen and forms a solution of bismuth-oxide.—¶ According to Arppe, bismuthic acid is distinguished from all other oxygen-compounds of bismuth by being converted into the green oxide, $BiO^3,3BiO^5$, when boiled with nitric acid. ¶—Cold hydrochloric acid gives off chlorine and forms a solution of bismuth-oxide. Aqueous hydriodic acid forms brown iodide of bismuth and evolves iodine. Oxalic, tartaric, citric, and acetic acid do not act upon bismuthic acid even at a boiling heat; but if sulphuric acid be added, solution takes place with violent effervescence. Aqueous alkalis have no action on it. (A. Stromeyer.)

Combinations.—¶ *a.* With Water.—*Hydrate of Bismuthic Acid.*—Obtained, when bismuth-oxide (prepared by boiling the hydrated oxide with potash) is briskly boiled with a very strong solution of potash, and chlorine passed through the mixture. The oxide soon acquires a fine red colour, and is converted into the hydrated acid. The compound thus formed is mixed, however, with a considerable quantity of potash and with the lower oxides of bismuth: from these it may be freed by washing with water, then digesting in dilute nitric acid, and finally washing with boiling water. It contains: bismuth 81·26, oxygen 15·48, water 3·26, corresponding to the formula BiO^5,HO. (Arppe.) ¶

b. With Salifiable Bases.—*Bismuthates.*—Bismuthic acid combines with potash (Arppe), and forms a few double salts, the bases of which are bismuth-oxide and an alkali.

BISMUTH AND HYDROGEN.

Hydride of Bismuth?—When the negative electricity of a voltaic battery is conducted into water by a bismuth pole, the bismuth immediately blackens and becomes covered with black dendrites. (Ruhland, *Schw.* 15, 417.)—¶ Meurer (*Arch. Pharm.* 2nd series, 36, 33) states that a gaseous compound of bismuth and hydrogen is obtained by the action of zinc on aqueous hydrochloric or sulphuric acid containing chloride of bismuth. This statement has however been disproved by Schlossberger & Fresenius. (*Ann. Pharm.* 51, 418.) ¶

BISMUTH AND CARBON.

CARBONATE OF BISMUTH-OXIDE.—By double decomposition. White powder, not soluble either in water or in aqueous carbonic acid: contains less than 1 At. carbonic acid.—¶ It contains exactly 1 At. carbonic acid. (Heintz, Lefort.)—When a bismuth-solution is mixed with an alkaline bicarbonate, a precipitate is formed, consisting of BiO^3,CO^2+HO. (Lefort, *Compt. rend.* 27, 268.) ¶

BISMUTH AND BORON.

BORATE OF BISMUTH-OXIDE.—White, very heavy powder, insoluble in water.

BISMUTH AND PHOSPHORUS.

A. **PHOSPHIDE OF BISMUTH.**—The metal takes up but a small quantity of phosphorus; the resulting compound exhibits before the blowpipe a small greenish flame. (Pelletier.) Bismuth, by combining with phosphorus, is rendered more brittle and less laminar. (Marx, *Schw.* 58, 471.) Phosphuretted hydrogen gas throws down from nitrate of bismuth-oxide a black phosphide of bismuth, which gives off all its phosphorus by distillation. (Berzelius; *comp.* Landgrebe, *Schw.* 55, 100.)

B. Phosphite of Bismuth-oxide.—Terchloride of phosphorus dissolved in water and neutralized by ammonia, gives with a solution of bismuth-oxide in hydrochloric acid—if the acid has been neutralized with ammonia as far as possible without precipitation—a copious white precipitate, which, when heated in a retort, gives off pure hydrogen gas. (H. Rose.)

C. Ordinary Phosphate of Bismuth-oxide; Bismuth-phosphate.—Aqueous phosphoric acid forms with hydrated oxide of bismuth either a white, insoluble powder which fuses to a white enamel, or a crystalline salt soluble in water. (Wenzel.)

D. Pyrophosphate of Bismuth-oxide.—This salt, which is precipitated from bismuth-salts by pyrophosphate of soda, is soluble in excess of the latter. (Stromeyer.)—¶ Schwarzenberg, by adding pyrophosphate of soda to a solution of bismuth-nitrate mixed with acetic acid, obtained a white, amorphous, bulky precipitate, which, in the course of 24 hours, was converted into a heavy, crystalline powder. This, when examined by the microscope, was found to consist of two different kinds of crystals. When bismuth-oxide was boiled with acid pyrophosphate of soda, a considerable quantity dissolved. (*Ann. Pharm.* 65, 160.) ¶

E. Metaphosphate of Bismuth-oxide.—Formed by mixing a solution of the nitrate, first with metaphosphoric acid, and then with ammonia. The precipitate is not soluble in excess of ammonia. (Persoz.)

Bismuth and Sulphur.

A. Bisulphide of Bismuth.—The sulphide of bismuth described by Gregers Klack, appears to have this composition. (Berzelius, Löthrohr, 136.)—Bismuth may be fused in any proportion with the tersulphide. (Lagerhjelm, Werther.) When a fused mixture of equal parts of these substances is left to cool, the bisulphide crystallizes out first, carrying with it the nickel and copper contained in the commercial bismuth; the liquid metal may then be poured off.—If 10 parts of purified bismuth be fused with 3 parts of sulphur in a crucible, the resulting mixture again fused three times with fresh sulphur in an assay-crucible, and then quickly cooled, a radiated mass is obtained, having a nest of crystals in its interior.—Square prisms, with truncated lateral edges (*Fig.* 31, without the *e-faces*); very thin and long crystals, with shining surfaces. Specific gravity 7·29. Whitish-grey, with strong metallic lustre; fuses more easily than the tersulphide. When heated out of contact of air, it does not give off sulphur till the temperature is raised very high, and even then the quantity sublimed does not exceed a mere trace. When heated in the air, it gives off sulphurous acid. (Werther, *J. pr. Chem.* 27, 65; abstr. *Pogg.* 57, 481.)

			Werther.		Wenzel.	Heintz.
			Crystals.	*Radiated mass.*		
Bi	213	86·93	86·20	86·34	85	86·20
2S	32	13·07	13·81	13·50	15	13·72
BiS^2	245	100·00	100·01	99·84	100	99·92

That the sulphide of bismuth prepared by Werther, is really BiS^2, is shown by its greater density and by the analysis. It is, however, remarkable, that BiS^2 and BiS^3 should have (as they appear to have) the same crystalline form. At all events, it seems that the fusion of bismuth with sulphur may likewise yield the tersulphide, as indeed is indicated by the analyses of artificial sulphide of bismuth by Lagerhjelm and John Davy, given below.

B. TERSULPHIDE OF BISMUTH.—Found native as *Bismuth-glance.*—Formed by fusing together the elements which compose it. Precipitated in brown-black flakes on mixing bismuth-salts with hydrosulphuric acid or an alkaline hydrosulphate.—Both the native and the artificial varieties belong to the right prismatic system. Right rhombic prisms, truncated at the edges, *Fig.* 73, but having merely the *p*-faces instead of acumination-faces; $u' : u = 91°$; $m : t$, 134° 30′. Cleavage distinct parallel to *t*, indistinct parallel to *p* and *u*. (W. Phillips, *Phil. Mag. Ann.* 2, 81; also *Pogg.* 11, 476.) Specific gravity of the native variety, 6·4....6·5; specific gravity of the sulphide precipitated by sulphuretted hydrogen, and then fused [with loss of sulphur?] out of contact of air, 7·001. (Karsten.) Colour, light lead-grey. Fuses less easily than bismuth. The artificial variety expands forcibly as it solidifies after fusion. (Marx.)

			Lagerhjelm. *Artificial.*	J. Davy. *Artificial.*	H. Rose. Riddarhyttan.
Bi	213	81·61	81·62	81·8	80·98
3S	48	18·39	18·38	18·2	18·72
BiS^3	261	100·00	100·00	100·0	99·70

At each successive fusion of the artificial sulphide, globules of metallic bismuth separate from the solidifying mass. (Marx, *Schw.* 58, 472; 59, 114.) The native tersulphide, heated in a tube, yields sublimed sulphur; on charcoal, before the blowpipe, it fuses with ebullition, and leaves metallic bismuth. (Berzelius.) By the addition of carbonate of soda, the bismuth is easily reduced before the blowpipe. Nitric acid dissolves the metal from the sulphide, with separation of sulphur.—When vapour of water is passed over red-hot sulphide of bismuth, sulphuretted hydrogen is evolved, and bismuth-oxide with a small quantity of metal, left behind. (Regnault.) Hydrogen gas converts red-hot sulphide of bismuth into sulphuretted hydrogen and metallic bismuth; and phosphuretted hydrogen at a gentle heat, produces sulphuretted hydrogen, phosphorus and metallic bismuth. (H. Rose.) [On the behaviour of tersulphide of bismuth with litharge, *vid.* Berthier, *Ann. Chim. Phys.* 39, 249.]

C. SULPHITE OF BISMUTH-OXIDE OR BISMUTH-SULPHITE.—Aqueous sulphurous acid forms, with hydrated bismuth-oxide, a salt which is not soluble either in water or in aqueous sulphurous acid; when heated somewhat strongly, it gives off its acid. (Fourcroy.)

D. SULPHATE OF BISMUTH-OXIDE OR BISMUTH-SULPHATE.—*a.* Monosulphate.—1. By decomposing the tersulphate *c* with water. (Gay-Lussac.)—¶ 2. By dissolving bismuth-oxide in sulphuric acid, evaporating to dryness, and gently heating the residue till it turns yellow. (Heintz.) ¶—White powder insoluble in water.—White when cold, yellow when heated. (Heintz.) ¶ Gives off sulphurous acid and oxygen when heated. (Gay-Lussac.)

			Berzelius.	Heintz.	
BiO^3	237	85·56	85·5	84·88	86·59
SO^3	40	14·44	14·5	15·12	13·34
BiO^3,SO^3	277	100·00	100·0	100·00	99·93

This salt is likewise obtained, in combination, however, with 2 atoms of water, by washing the bisulphate *b* with water. (Heintz.)

¶ *Bisulphate.*—Separates in small delicate needles when a solution of bismuth-nitrate in nitric acid is mixed with sulphuric acid. When strongly heated, it gives off water and sulphuric acid, and is converted into the preceding salt. Water likewise decomposes it: the crystals must therefore be purified not by washing with water, but by pressure between bibulous paper. (Heintz.) ¶

			Heintz.		
BiO^3	237	68·85	68·40	68·36	68·38
$2SO^3$	80	23·30	23·79	24·16	24·12
$3HO$	27	7·85	7·81	7·48	8·05
$BiO^3,2SO^3 + 3Aq.$	344	100·00	100·00	100·00	100·55

c. Tersulphate.—Remains in the form of a white mass when bismuth is heated with oil of vitriol, sulphurous acid and even sulphur being evolved. According to Arfvedson, it is reduced to the metallic state when heated to redness in hydrogen gas. Water resolves it into *a*, which remains undissolved, and *c*, which dissolves.

			Lagerhjelm.	Thomson.
BiO^3	237	66·39	66·35	66·67
$3SO^3$	100	33·61	33·65	33·33
$BiO^3,3SO^3$	357	100·00	100·00	100·00

d. Acid Sulphate.—The aqueous solution when evaporated, yields needle-shaped crystals, and afterwards a dry deliquescent mass of salt, which, according to Gay-Lussac, evolves hydrated sulphuric acid when heated.

E. SULPHIDE OF CARBON AND BISMUTH.—Hydrosulpho-carbonate of lime yields with bismuth-salts a dark brown pecipitate, which, when added in excess, it dissolves, forming a red-brown solution. (Berzelius.)

BISMUTH AND SELENIUM.

SELENIDE OF BISMUTH.—The two substances, when heated together, unite with faint evolution of light and heat, and form a silver-white mass, having a crystalline fracture, and fusing at a red heat; the fused mass has a specular surface. (Berzelius.)

BISMUTH AND IODINE.

A. IODIDE OF BISMUTH.—*a. With a small proportion of Iodine.*—A mixture of equal parts of bismuth and iodine [about 1 At. metal to 1½ At. iodine] fuses when heated, and sublimes even below its melting point, in laminæ having the metallic lustre. Water boiled with the compound turns yellow and sour, and leaves brown oxy-iodide of bismuth. (Berthemot, *J. Pharm.* 14, 616.) On heating a mixture of 213 parts (1 At.) of bismuth and 378 parts (3 At.) iodine, heat is evolved, a large quantity of iodine volatilizes, and a grey, brittle mass is formed, from which water takes up a small quantity of hydriodic acid, but no bismuth. (Rammelsberg.)

TERIODIDE OF BISMUTH.—Formed by precipitating a bismuth-salt with iodide of potassium. The bismuth-salt may be kept clear by means of acetic acid, or it may be first mixed with hydrochloric acid, then precipitated by water, and the iodide of potassium afterwards added; for that salt likewise decomposes the basic hydrochlorate of bismuth-oxide. The yellow filtrate contains in solution a small quantity of iodide of bismuth.

Brown crystalline precipitate. Partially decomposed during washing, but may be dried without difficulty. (Rammelsberg, *Pogg.* 48, 166.)

			Rammelsberg.	
Bi	213	36·04	36·02	37·10
3I	378	63·96		
BiI^3	591	100·00		

¶ According to Arppe, the iodide obtained by dropping a solution of nitrate of bismuth-oxide into a solution of iodide of potassium is contaminated with nitrate of bismuth-oxide; but when a solution of iodide of bismuth in hydriodic acid is diluted with water, a precipitate is formed, consisting of pure BiI^3. ¶

B. OXY-IODIDE OF BISMUTH.—The chestnut-brown powder which remains undissolved when iodide of bismuth, *a*, is boiled with water. Zinc and iron decompose it on continued boiling with water. A concentrated solution of potash or soda, or strontia-water decomposes completely with separation of bismuth-oxide; dilute solutions of potash and soda, even when heated, and likewise aqueous carbonate of potash or soda, baryta-water, and lime-water, decompose it but partially. (Berthemot.) Red powder, completely insoluble in water. Consists of BiI^3+2BiO^3. (Arppe.)

¶ C. IODIDE OF BISMUTH AND HYDROGEN.—$BiI^3+HI+8Aq$.—Separates, in octohedral crystals with rhombic base, when a solution of iodide of bismuth in hydriodic acid is evaporated over sulphuric acid. These crystals are decomposed by water, without separation of iodine, but are completely dissolved by iodide of potassium. (Arppe.) ¶

D. IODATE OF BISMUTH-OXIDE or BISMUTH IODATE.—Iodic acid and iodate of potash give with nitrate of bismuth, a white precipitate insoluble in water. (Pleischl.) When a solution of nitrate of bismuth is precipitated by water, and the liquid filtered from the precipitated mononitrate is mixed with iodate of soda, a copious white precipitate is obtained, insoluble in water, and very difficultly soluble in nitric acid. This precipitate, when dried at 100°, contains no combined water, and when heated in a retort, is resolved into oxygen gas, iodine vapour, and 39·65 per cent. of fused residue. The latter contains about 5 At. teroxide of bismuth for 1 At. teriodide. (Rammelsberg, *Pogg.* 44, 568.)

BISMUTH AND BROMINE.

A. BROMIDE OF BISMUTH.—Bismuth does not combine with bromine so readily or with so much development of heat as antimony. The compound is formed by heating the pulverized metal with a large excess of bromine in a long tube sealed at the end. The excess of bromine evaporates, together with a small quantity of bismuth; and the bromide of bismuth remains at the bottom of the tube in the form of a steel-grey substance which resembles fused iodine, melts at 200°, forming a hyacinth-red liquid, and boils when heated nearly to low redness. It absorbs moisture from the air, and is thereby converted into the sulphur-yellow hydrated bromide of bismuth. By large quantities of water, it is resolved into pure aqueous hydrobromic acid, and precipitated oxy-bromide of bismuth. (Serullas, *Ann. Chim. Phys.* 38, 323; abstr. *Pogg.* 14, 113.)

B. BROMATE OF BISMUTH-OXIDE OR BISMUTH BROMATE.—Freshly precipitated hydrate of bismuth-oxide, left in contact for a long time with aqueous bromic acid, yields the undissolved salt *a* and the dissolved salt *b*.—*a. Sesquibasic Salt.*—White, amorphous powder, which gives off its water between 150° and 160°, and is decomposed with violence at high temperatures, leaving yellow oxy-bromide of bismuth. (Rammelsberg.)

	Hydrated.		Rammelsberg.
$3BiO^3$	711·0	70·97	70·82
$2BrO^5$	236·8	23·64	23·39
$6HO$	54·0	5·39	5·79
$3BiO^3, 2BrO^5 + 6Aq.$	1001·8	100·00	100·00

b. The acid solution evaporated over the water-bath ultimately gives off bromine and oxygen gas, and leaves a small quantity of a salt which deliquesces in the air. (Rammelsberg, *Pogg.* 55, 76.)

BISMUTH AND CHLORINE.

A. CHLORIDE OF BISMUTH.—*Butter of Bismuth.*—1. Pulverized bismuth thrown into chlorine gas at ordinary temperatures burns with a pale blue light, and forms chloride of bismuth.—2. The chloride is likewise formed by heating 1 part of bismuth with 2 parts of corrosive sublimate.—3. By evaporating hydrochlorate of bismuth-oxide to dryness and distilling the residue out of contact of air.—Brownish or greyish-white; opaque; with granular fracture; fuses very easily, forming an oily liquid (J. Davy); volatilizes at a moderate heat. (H. Davy.) Vapour-density = 11·35. (Jacquelain.) When distilled in vessels containing air (not in vessels containing carbonic acid), it yields a small quantity of oxychloride of bismuth in micaceous laminæ. (Jacquelain.) Decomposed by oil of vitriol, but only at high temperatures, and then with violent effervescence, yielding hydrochloric acid gas and sulphate of bismuth-oxide. (A. Vogel.) Water converts it into hydrochloric acid holding a small quantity of bismuth-oxide in solution, and oxychloride of bismuth.

			J. Davy.
Bi	213·0	66·73	66·4
3Cl	106·2	33·27	33·6
$BiCl^3$	319·2	100·00	100·0

	Vol.	Sp. gr.	Vol.	Sp. gr.
Bismuth vapour?	1	29·5344 =	$\frac{1}{4}$	7·3836
Chlorine gas	6	14·7258 =	$1\frac{1}{2}$	3·6814
Vapour of Chloride of Bismuth	4	44·2602 =	1	11·0650

Hydrated Chloride of Bismuth or *Ter-hydrochlorate of Bismuth-oxide.*—Separates in prisms, when a solution of acid hydrochlorate of bismuth-oxide is evaporated. Water resolves it into oxychloride of bismuth, and dilute hydrochloric acid holding bismuth-oxide in solution.

B. Oxychloride of Bismuth.—*Basic Hydrochlorate of Bismuth-oxide.*—1. Formed by passing vapour of water over melted chloride of bismuth, and afterwards expelling the unaltered chloride by the application of a stronger heat.—2. By distilling chloride of bismuth in vessels containing air.—3. By decomposing chloride of bismuth with water, and washing the precipitate.—4. By precipitating a solution of bismuth-nitrate with common salt, chloride of potassium, or hydrochloric acid not too much diluted. An excess of the solution of chloride of potassium redissolves the precipitate; but after the precipitate has been washed and dried, the same liquid no longer dissolves it. (Bucholz.)

White, crystalline, becoming yellow whenever it is heated (Jacquelain); fuses at a red heat without decomposing. (Grouvelle, Jacquelain.) Hot oil of vitriol converts it into sulphate of bismuth-oxide. By chlorine at a red heat it is converted into oxygen gas and chloride of bismuth, which volatilizes without residue. Potash, when hot and concentrated, converts it into bismuth-oxide and chloride of potassium. (Jacquelain.) The separated oxide, though free from chlorine, is not yellow but greyish-black, and retains that colour when feebly ignited; when fused, however, it turns yellow. (Phillips, *Phil. Mag. Ann.* 8, 406; also *Br. Arch.* 39, 41.) Dilute solution of potash, even on boiling, extracts no chlorine from it (A. Stromeyer, Jacquelain), or only a portion of that which it contains. (Warington, *Phil. Mag. Ann.* 9, 30.) Dissolves in hot nitric acid, and is left behind unchanged when the acid is evaporated. (Jacquelain.) Dissolves in hydrochloric acid, forming a solution of C. Totally insoluble in water. (H. Rose.)

			Jacquelain.	Phillips.	Arppe.
3Bi	639·0	80·56	79·95	78·19	81·44
3Cl	106·2	13·39	13·45	13·32	13·43
6O	48·0	6·05	6·60		5·13
$BiCl^3,2BiO^3$	793·2	100·00	100·00		100·00

Or:

$BiCl^3$	319·2	40·24
$2BiO^3$	474·0	59·76
	793·2	100·00

¶ When this compound is exposed to a high temperature, it is resolved into neutral chloride of bismuth, which volatilizes, and a residual salt with excess of base, which appears to be composed of $BiCl^3 + 6BiO^3$. (Arppe.) According to Heintz, the oxychloride obtained by treating the hydrochloric acid solution with water contains an atom of water: $BiCl^3,2BiO^3+HO$. ¶

C. AQUEOUS HYDROCHLORATE OF BISMUTH-CHLORIDE, or ACID HYDROCHLORATE OF BISMUTH-OXIDE.—Formed by dissolving the metal in aqua-regia, or the chloride or oxide in hydrochloric acid. The colourless solution, provided it does not contain too great an excess of acid, deposits the compound B on the addition of water. With protochloride of tin, it gives, according to A. Vogel, a siskin-green precipitate.

BISMUTH AND FLUORINE.

FLUORIDE OF BISMUTH.—Deposited in the form of a white powder, when the aqueous solution is evaporated. (Berzelius.)

BISMUTH AND NITROGEN.

A. NITRATE OF BISMUTH-OXIDE or BISMUTH-NITRATE.—*a. Mononitrate.*—Basic Nitrate of Bismuth, Bismuth-white, White cosmetic, Pearl-white, Magistery of Bismuth, Magisterium Bismuthi, Blanc d'Espagne.—Formed by decomposing *b* or *c* with water or with an insufficient quantity of alkali; or by boiling *c* with excess of bismuth—or by heating the ternitrate *b* to 148·7° (300° F.) for some hours. (Gladstone.) The usual mode of preparation is to saturate warm dilute nitric acid with bismuth—which, to free it from arsenic, must be previously fused with $\frac{1}{16}$ of its weight of nitre (*J. Pharm.* 18, 688)—then dilute with a quantity of water sufficient to prevent the corrosive action of the acid upon paper, but not to produce a permanent precipitate—pass the liquid through a double filter—and precipitate by a quantity of water, weighing from 30 to 100 times as much as the bismuth contained in the solution. If the quantity of water is too small, the precipitation is not complete; if it is too large, a small portion of the precipitate redissolves. The precipitate is thrown on a filter, washed several times with cold water, and dried between bibulous paper. The filtrate, when warm, deposits slender crystals,—but, according to Duflos, only when the nitric acid contains hydrochloric acid; a mere trace of the latter is however sufficient to produce the effect. Common salt, according to Phillips, precipitates oxychloride of bismuth from the filtrate. Duflos, (*Schw.* 68, 191; *N. Br. Arch.* 23, 307) dissolves 1 part of the crystals of salt *b* in 2 or 3 parts of warm water; filters to separate any insoluble residue of bismuth-arseniate; pours the filtrate into 24 times its bulk of hot water, stirring all the while; leaves the precipitate to subside, and decants the liquid; then agitates the deposit with a fresh quantity of water; again leaves it to subside and decants; and finally dries the precipitate on a brick between many folds of bibulous paper. The preparation thus obtained is free from arsenic. Ordinary magistery of bismuth frequently contains arsenic. In that case it yields arseniuretted hydrogen, when treated with zinc and hydrochloric acid in Marsh's apparatus. (Chevallier, *J. Pharm.* 15, 383; Reinsch, *Repert.* 64, 206.)

Very soft, silky needles and scales, or—when prepared from the crystals—loosely coherent powder having a faint pearly lustre. Reddens moistened litmus-paper. If washed too long with water, especially with hot water, it is converted into a more basic salt. (Herberger; Buchner, *Repert.* 55, 289, and 306.) When ignited, it leaves teroxide of bismuth.

With protochloride of tin, it assumes an orange-yellow colour, which, after some days, or immediately on boiling, changes first to brown and afterwards to black. (A. Vogel; *vid. Suboxide of Bismuth*, p. 429.) Slightly, if at all, soluble in water, which, according to Duflos, extracts from it a more acid and leaves a more basic salt. It does not blacken in sunlight, unless it contains chloride of silver (Klaproth, Busch. *Br. Arch.* 24, 341), or unless portions of filter-paper are attached to it. (Wittstein, *Repert.* 74, 243.)

			Herberger.	Duflos.	Grouvelle.	Phillips.	Ménigaud. *Dried at* 100°.
BiO^3	237	79	79·70	80·00	81·37	81·92	85·33
NO^5	54	18	14·44	13·58	13·97	18·36	14·67
HO	9	3	5·86	6·42	4·66		
$BiO^3, NO^5 + Aq.$	300	100	100·00	100·00	100·00	100·28	100·00

Magistery of bismuth, obtained by precipitating with water the solution of the crystallized salt *b* in nitric acid, and dried for several weeks, by heating it over the water-bath during the day and placing it under a receiver with oil of vitriol at night—whereby its weight was slowly but continuously diminished—was found by the author to contain 80·67 per cent. bismuth-oxide, 2·92 water, and therefore 16·41 nitric acid. The water was determined by passing the aqueous vapour, evolved by heating the substance in a glass tube, first over ignited metallic copper, and then into a tube containing chloride of calcium; the water thus collected was inodorous. Even though the quantity of bismuth-oxide found in this analysis should be rather too great—inasmuch as the salt may have been partially decomposed by the prolonged heating to which it was subjected in drying—the experiment proves at least that the salt, when dried at 100°, contains water as an essential constituent, contrary to the results obtained by Phillips and Ménigaud. ¶ Gladstone finds that the salt obtained by heating the crystallized nitrate *b* to 300°, likewise contains one atom of water. His analysis gives,—bismuth-oxide, 79·23 per cent.; nitric acid, 18·49; water (mean of four experiments), 3·22. The water was determined in the manner just described; the nitrogen by the *absolute* method used in organic analysis, and the nitric acid calculated therefrom; and the bismuth-oxide, by igniting the salt in a platinum crucible.

The composition and properties of the basic nitrates of bismuth-oxide have lately been examined by Becker, (*Arch. Pharm.* 55, 31, and 129; abstr. *Ann. Pharm.* 68, 282), whose results differ considerably from those above detailed. He finds that the basic nitrate, directly obtained by treating the ternitrate with cold water, contains 2 atoms of water, and that it has invariably the same composition, whether the ternitrate from which it is formed is in the state of crystals or of a very acid solution; and, further, that the same basic salt is obtained by digesting metallic bismuth in the concentrated acid solution of the ternitrate. The composition of this basic nitrate is as follows:—

			Becker.		
			a.	*b.*	*c.*
BiO^3	237	76·65	77·33	77·51	77·47
NO^5	54	17·53	17·20	17·23	17·09
2HO	18	5·82	5·47	5·26	5·44
$BiO^3, NO^5 + 2Aq.$	309	100·00	100·00	100·00	100·

a and *b* were precipitated by water; *c* was obtained by digesting pulverized bismuth in the nitric acid solution. The bismuth-oxide and nitric acid were determined directly, the water by loss.—The salt, when heated to 100°, loses half its water, as previously shown by Heintz.

When freshly precipitated, this salt is somewhat freely soluble in water, especially if the water contains nitric acid. Hence if, after the precipitation of the basic salt, the supernatant liquid be mixed with a large quantity of water, the precipitate is completely redissolved; but, after a time, the length of which depends upon the temperature and the quantity of acid present, a basic salt separates out. If the solution contained free nitric acid, and the water added was cold, the salt thus separated consists of $5BiO^3,4NO^5+9Aq$. This, according to Becker, is the true *magistery of bismuth*, inasmuch as, according to the usual directions for preparing that substance, (see page 440) the same change takes place in washing the precipitate on the filter. A portion of the precipitate is, however, dissolved during the washing, and separates when the filtered liquid is left at rest for a while. The disappearance of the precipitate during washing is however occasioned, not so much by actual solution, as by the mechanical condition of the precipitated mononitrate, which, in fact, consists of very soft and light laminæ, easily washed away by the water, whereas the true *magistery* forms thick, short prisms. To avoid loss, it is, therefore, advisable to wash the precipitate by decantation, after pouring off the acid liquid. The analysis of magistery of bismuth, obtained as above, gave the following results:

			Becker.	
$5BiO^3$	1185	79·91	79·85	80·18
$4NO^5$	216	14·62	14·52	14·58
$9HO$	81	5·47	5·63	5·26
$5BiO^3,4NO^5+9Aq.$	1482	100·00	100·00	100·02

This analysis agrees very nearly with that of Herberger, given on page 441; the latter is, therefore, more accordant with the formula just given than with that of the mononitrate, or with that which Herberger himself assigned, viz., $4BiO^3,3NO^5+9Aq$.

Magistery of bismuth is not sensibly soluble in cold water, but the water extracts acid and a small quantity of oxide from it; hot water converts it into a heavy dingy-coloured powder. The powder which remains after long boiling, still retains 1 per cent. of nitric acid, which cannot be completely extracted by water.

A salt containing the same proportions of base and acid, but with 12 atoms of water, is obtained by evaporating a concentrated solution of the ternitrate at a strong heat: the salt then separates in crystalline crusts, which, when pressed between bibulous paper, are reduced to a very hard, shining, crystalline powder. It contains 78·49 BiO^3, 13·96 NO^5, and 7·55 water, corresponding to the formula $5BiO^3,4NO^5+12Aq$.

If the precipitate first obtained by the action of cold water on a solution of the ternitrate, be heated in contact with a free acid—or if the same acid solution be poured into hot water—a white, very loose powder is precipitated, containing 80·24 BiO^3, 15·43 NO^5, and 4·33 water, which corresponds to the formula $6BiO^3,5NO^5+9Aq$.—This salt is decomposed by water more readily than the magistery of bismuth. If it be washed with water as long as the filtrate continues to exhibit a strongly acid reaction, the residue then left consists of prisms of unequal magnitude, and forms a heavy and not perfectly white powder. It consists of $4BiO^3, 3NO^5+9Aq.$, and is, therefore, identical with the magistery of bismuth obtained by the method of Duflos.

Lastly, if the mononitrate, completely freed from the adhering acid liquid, be treated with water likewise free from acid, it dissolves completely; but the liquid, after a while, becomes milky, and, after long standing, deposits a white, amorphous powder, containing $5BiO^3, 3NO^5+8Aq$. This salt may be formed, in addition to the true magistery of bismuth, if too large a quantity of water be used and the greater part of the acid liquid removed. ¶

b. Ternitrate.—Formed by dissolving the metal in hot nitric acid, evaporating the solution, and leaving it in a cold place.—Transparent and colourless, oblique six-sided and eight-sided prisms, terminated with several faces; the crystals appear to belong to the doubly oblique prismatic system. At 100°, they separate into a solid and a liquid portion; the latter solidifies suddenly on cooling. (Graham.) When distilled, they give off hydrated nitric acid, and leave first the mononitrate *a* and afterwards the pure oxide. (Berzelius.) When exposed to the air at 87°, they give off so much water and acid, that they are reduced to a basic salt, and, if afterwards heated to 260°, sustain scarcely any further loss. The total loss amounts to 32·47 per cent., and there remains 67·53 per cent. of salt *a* (Graham, *Ann. Pharm.* 29, 16.) [These numbers are not exact, as Liebig correctly remarks.] ¶ According to Gladstone, the crystals, when heated to 150°, are reduced to $BiO^3, NO^5+Aq.$ (*vid.* p. 440) and this when heated to 260°, gives up its acid and water. ¶—The crystals, when thrown on red-hot coals, detonate slightly and emit red sparks; these effects are produced in greater intensity on rubbing the crystals with phosphorus. (Brugnatelli.)—Dilute nitric acid dissolves them completely; pure water only partially, the solution consisting of salt *c*, while *a* remains undissolved. A small quantity of water produces less of the salt *a*, and the resulting solution treated with more water gives a fresh precipitate. With a sufficient quantity of water (according to Grouvelle, *Ann. Chim. Phys.* 19, 141), 100 parts of the crystals yield about 54 parts of salt *a*. With 50 parts water, 100 parts of the crystals yield 16 parts of salt *a*; with 100 water, 18; with 200 water, 27; with 400 water, 32; with 800 water, 39; with 1,200 water, 43; and with 1,600....12,800 water, 45 parts of salt *a*. (Duflos.) The liquid obtained with 1,600 ...12,800 water, becomes turbid if warmed after filtering, and deposits crystalline scales of salt *a*.

		Crystallized.	Duflos.	Berzelius.	Graham
BiO^3	237	49·38	48·3	48·8	49·49
NO^5	162	33·75	33·5	33·7	
9HO	81	16·87	18·2	17·5	
$BiO^3, NO^5+9Aq.$	480	100·00	100·0	100·0	

		Crystallized.	Gladstone.
BiO^3	237	48·46	48·15
$3NO^5$	162	33·13	32·38
10HO	90	18·41	19·47
$BiO^3, 3NO^5+10Aq.$	489	100·00	100·00

c. Aqueous Acid Nitrate of Bismuth-oxide.—Obtained by dissolving bismuth or bismuth-oxide, or salt *a*, or salt *b*, in nitric acid. The stronger the acid, the greater is the quantity of bismuth that the solution can contain; water precipitates from it the salt *a*, provided the acid is not in very great excess. The solution, after precipitation with a large quantity of water, still retains 7 parts of bismuth-oxide to 19·15 nitric acid $=1$ At. $BiO^3 : 12NO^5$; if this liquid be so gently evaporated that no nitric acid is given off from it, there remains a non-crystallizable syrup, which mixes with water without turbidity. (Duflos.) Acetic acid added to a solution of bismuth in nitric acid prevents the precipitation by water.

Freshly precipitated bismuth-oxide is not perceptibly soluble in caustic ammonia or carbonate of ammonia (p. 431).

B. AMMONIO-IODIDE OF BISMUTH.—100 parts (1 At.) of iodide of bismuth, heated in a stream of ammoniacal gas, take up 9·505 parts (rather more than 3 At.) of ammonia, and are converted into a brick-red mass, which, when treated with water, gives up hydriodate of ammonia, without change of colour. (Rammelsberg.)

C. AMMONIO-CHLORIDE OF BISMUTH.—Chloride of bismuth, when gently heated, absorbs ammoniacal gas.

D. CHLORIDE OF BISMUTH AND AMMONIUM.—A solution of 319·2 parts (1 At.) of chloride of bismuth, and 106·2 parts (2 At.) of sal-ammoniac, yields on evaporation, double six-sided pyramids, isomorphous with those of chloride of antimony and ammonium (p. 374). (Jacquelain.)

		Crystallized.	Jacquelain.	Or:		
$2NH^4$	36	8·45		$2NH^4Cl$	106·8	25·07
Bi	213	50·00	49·78	$BiCl^3$	319·2	74·93
5Cl	177	41·55	41·89			
$2NH^4Cl+BiCl^3$	426	100·00			426·0	100·00

¶ A solution of 6 At. sal-ammoniac and 1 At. chloride of bismuth yields tabular rhombic crystals containing $3NH^4Cl+BiCl^3$. (Arppe.) ¶

The hydrate, carbonate, phosphate, and mononitrate of bismuth-oxide, when freshly precipitated, dissolve readily in sal-ammoniac but not in nitrate of ammonia. (Brett, *Phil. Mag. J.* 10, 98 and 335.)

BISMUTH AND POTASSIUM.

A. BISMUTHIDE OF POTASSIUM.—*a.* Four volumes of bismuth-powder combine readily with one volume of potassium, at the melting-point of the latter, and form a brittle, easily fusible mixture, of fine laminar texture: it oxidates when exposed to the air—dissolves with effervescence in water—and still more readily in dilute acids. (Gay-Lussac & Thénard.) The combination is attended with development of light and heat. The resulting compound is tin-white and fine-grained; does not expand in solidifying from a state of fusion; perforates an iron spoon in which it is melted. (Marx, *Schw.* 58, 463.)—*b.* An alloy of bismuth and potassium may likewise be formed by heating very strongly for two hours in a covered crucible, a mixture of equal parts of bismuth and cream of tartar covered with lamp-black (Vauquelin, *Schw.* 21, 221); or of 120 parts bismuth, 60 parts of cream-of-tartar carbonized and somewhat roasted, and 1 part of nitre. (Serullas, *Ann. Chim. Phys.* 21, 200.) The alloy obtained by the process of Serullas emits sparks when cut with the shears; fuses and burns vividly when broken up; and when thrown on mercury covered with water, moves about with great rapidity. (Serullas.)

¶ B. BISMUTHATE OF POTASH.—$KO,2BiO^5+Aq$.—Hydrated bismuthic acid is somewhat soluble in boiling caustic potash. Acids added to the colourless solution throw down a white or reddish precipitate, the insoluble red portion of which is the salt having the composition above stated. (Arppe.)

C. SULPHATE OF BISMUTH-OXIDE AND POTASH.—$BiO^3,3SO^3+3KO,SO^3$.—Obtained by adding sulphate of potash in large excess to a very concentrated solution of bismuth-nitrate in nitric acid. If a dilute solution of bismuth be used, the precipitate appears to be a mixture of various salts. (Heintz.) ¶

D. BISMUTHATE OF BISMUTH-OXIDE AND POTASH.—*a. Ochre-yellow Salt.*—Formed by heating 5 parts of hydrate of potash in a silver crucible till it is reduced to a state of tranquil fusion, then adding 1 part of bismuth-oxide, and heating for a quarter of an hour, at a continually increasing temperature. The oxide turns greenish, and dissolves, in proportion as it becomes more highly oxidized by the oxygen which the potash absorbs from the air, forming a transparent, ochre-yellow liquid. This liquid, when slowly cooled, solidifies to a mass resembling *Aventurine,* and containing a great number of fine crystalline scales. Continued washing with water withdraws from the mixture the greater portion of the potash, and leaves the double salt (ochre-yellow, according to Bucholz & Brandes), mixed, however, with silver from the crucible. If too large a quantity of bismuth-oxide is used, a portion of it remains at the bottom of the crucible, crystallized in needles. (Jacquelain.)

			Or:			Jacquelain.
KO	47·2	2·39	KO	47·2	2·39	2·26
$6BiO^3$	1422·0	71·99	8Bi	1704·0	86·27	86·16
$2BiO^5$	506·0	25·62	28O	224·0	11·34	11·56
$KO,6BiO^3,2BiO^5$	1975·2	100·00			100·00	99·98

In Jacquelain's analysis, the silver mixed with the salt is deducted: he states that the salt likewise contains a small quantity of water.

This compound is permanent in the air. It gives off water at 125° and oxygen at 145°; and, at a red heat, is converted into a deliquescent mixture of bismuth-oxide and potash. In the preparation of this salt, it is probable that a compound richer in potash is first formed, and that this compound does not give off oxygen even when strongly ignited: it is however converted by washing into the compound containing a smaller quantity of potash. The salt when treated with very dilute nitric, sulphuric, or acetic acid, gives off oxygen gas. It dissolves instantly in melted hydrate of potash, whereas bismuth-oxide dissolves but slowly, in proportion as the oxygen of the air is absorbed by the potash and transferred to it. (Jacquelain.)

b. Brown Salt.—Bismuthate puce de Potasse.—To prepare this salt, bismuth-oxide obtained by igniting the nitrate is boiled for a long time with chloride of potash or soda, obtained by precipitating chloride of lime with carbonate of potash or soda, the boiling being continued till the oxide assumes first a brown-yellow and then a black-brown colour: the product is then washed with water. Hydrated bismuth-oxide oxidizes less quickly than the anhydrous oxide; nitrate of bismuth-oxide, even when the chloride of potash is mixed with excess of caustic potash, yields the compound contaminated with oxychloride of bismuth.—2. Six parts of bismuth-oxide, either hydrated or anhydrous, are diffused in a solution of 40 parts of potash-hydrate in 500 parts of water, and chlorine gas rapidly passed through it, in such quantity however that the potash may remain in excess, the liquid being agitated all the while, and kept at a temperature between 90° and 100°. The oxide turns brown in a few minutes, whereupon the liquid is boiled for a short time, the solid product washed by decantation, and then dried at 100°. Flea-brown powder.

	Calculation.	
KO	47·2	4·52
$2BiO^3$	474·0	45·35
$2BiO^5$	506·0	48·41
2HO	18·0	1·72
$KO,BiO^5 + 2BiO^3,BiO^5 + 2Aq$	1045·2	100·00

	Calculation.		Jacquelain.
KO	47·2	4·52	4·63
$4BiO^3$	948·0	90·70	89·86
4O	32·0	3·06	3·28
2HO	18·0	1·72	2·22
	1045·2	100·00	99·99

According to Jacquelain: $2KO,8BiO^4 + 5Aq$. ¶ Heintz, by suspending bismuth-oxide in a solution of potash so strong that it solidified on cooling, and passing chlorine through it, leaving the potash in excess however, obtained an ochre-yellow substance, which he regards as a compound of peroxide of bismuth with potash and water: $KO,2BiO^4 + 3HO$. ¶

c. Purple Salt.—Bismuthate pourpre de Potasse.—Formed by diffusing 6 parts of bismuth-oxide or its hydrate in a saturated solution of 40 parts of potash-hydrate in cold water, and passing chlorine through, as in *b*. The oxide first becomes ochre-yellow, and then brown-red. As soon as this latter change has taken place, the stream of chlorine is interrupted; the liquid boiled for a few minutes; then decanted boiling hot; and the deposit washed by decantation, first with alcohol and then with water. If water were used in the first instance, it would precipitate the bismuth-oxide held in solution by the carbonate of potash. Purple powder. (Jacquelain.)

KO	47·2	5·91
BiO^3	237·0	29·65
$2BiO^5$	506·0	63·31
HO	9·0	1·13
$KO, BiO^5 + BiO^3,BiO^5 + Aq.$	799·2	100·00

Or:			Jacquelain.
KO	47·2	5·91	5·22
3Bi	639·0	79·96	81·22
13O	104·0	13·00	12·18
HO	9·0	1·13	1·36
	799·2	100·00	99·98

According to Jacquelain: $2KO,7BiO^4 + 3Aq$.—which formula certainly accords better with the analysis.

¶ **E. Iodide of Bismuth and Potassium.**—$2KI,BiI^3+4HO$.—Obtained by mixing ter-iodide of bismuth with iodide of potassium in solution, and evaporating. Thin rhombic tables. When a solution of iodide of bismuth in hydriodic acid is mixed with iodide of potassium and evaporated, small, black, easily soluble crystals are obtained, which, when heated, give off iodine and are converted into a red substance containing $4KI+BiI^3$: the black crystals are probably $4KI+BiI^3+HI$. (Arppe.) ¶

F. Chloride of Bismuth and Potassium.—Formed by slowly evaporating an aqueous solution of 149·2 parts (2 At.) of chloride of potassium and 319·2 parts (1 At.) of chloride of bismuth, till a crystalline film forms on the surface, and leaving the solution to cool. Rhombic octohedrons. (Jacquelain.)

		Crystallized.	Jacquelain.
2K	78·4	15·27	15·22
Bi	213·0	41·49	41·70
5Cl	177·0	34·48	34·84
5HO	45·0	8·76	8·24
$2KCl, BiCl^3+5Aq.$	513·4	100·00	100·00

Or:

2KCl	149·2	29·06
$BiCl^3$	319·2	62·18
5HO	45·0	8·76
	513·4	100·00

¶ According to Arppe, the compound $2KCl,BiCl^3$ is likewise formed when 3 At. chloride of potassium and 2 At. bismuth-oxide are dissolved in hydrochloric acid and the solution evaporated. By proceeding in a similar manner with 2 At. chloride of potassium and 1 At. bismuth-oxide, the compound $3KCl,BiCl^3$ is produced. ¶

Bismuth and Sodium.

A. Bismuthide of Sodium.—4 volumes of bismuth-powder and 1 volume of sodium, heated above the melting point of the latter, unite and form a yellowish-grey, very brittle, fine-grained mass, which is less fusible than bismuth, oxidizes quickly in the air, and effervesces strongly with water and aqueous acids. (Gay-Lussac & Thénard.) The combination of 4 volumes of bismuth-powder and 1 volume of sodium takes place several degrees below the melting point of bismuth, and is attended with vivid combustion. The alloy has a steel-grey colour, inclining to tin-white, and a broadly laminar structure; fuses more readily than bismuth, and expands in solidifying from fusion, but less strongly than bismuth. When immersed in water or in aqueous acids, it liberates hydrogen for a short time only, and becomes covered with a black powder; if it be then fused a second time, it will again produce effervescence for a while, on immersion in water. (Marx, *Schw.* 58, 462.) This alloy may likewise be obtained by igniting bismuth with charred soap. (Serullas.)

B. Bismuthate of Bismuth-oxide and Soda.—Bismuth-oxide when fused with hydrate of soda or treated with soda-ley and chlorine, exhibits phenomena similar to those which are produced by fusing it with hydrate of potash or treating it with potash-ley and chlorine. (A. Stromeyer, Frémy.)

C. CHLORIDE OF BISMUTH AND SODIUM.—Obtained by evaporating and cooling an aqueous solution of 117·2 parts of chloride of sodium and 319·2 parts of chloride of bismuth. Ill-defined, deliquescent prisms. (Jacquelain.)

	Crystallized.		Jacquelain.
2Na	46·4	9·46	9·8
Bi	213·0	43·44	43·5
5Cl	177·0	36·09	35·8
6HO	54·0	11·01	10·9
$2NaCl, BiCl^3 + 6Aq$	490·4	100·00	100·0

Or:

2NaCl	117·2	23·90
$BiCl^3$	319·2	65·09
6HO	54·0	11·01
	490·4	100·00

¶ Arppe, by evaporating a solution of 3 At. chloride of sodium and 2 At. bismuth-oxide in hydrochloric acid, obtained a salt which crystallized in six-sided prisms with three-sided summits, and contained $2NaCl, BiCl^3 + 2Aq$. ¶

BISMUTH AND SILICIUM.

SILICIDE OF BISMUTH (*Bismuth-blende* or *Bismuthite* of Breithaupt)—which has a density of 6·909, a conchoidal or earthy fracture, a green or yellow colour and feeble lustre, and is opaque, appears from Kersten's analysis (*Pogg.* 27, 81), to be $BiO^3, 2SiO^2$,—but likewise contains manganic oxide, ferric oxide, phosphoric acid, and hydrofluoric acid. (*Compare* Hünefield, *Schw.* 53, 85; Breithaupt, *Schw.* 50, 307; 54, 237; Breithaupt & Plattner, *Pogg.* 53, 627.)

Bismuth-oxide dissolves in glass, and gives it a yellowish colour.

BISMUTH AND TUNGSTEN.

SULPHOTUNGSTATE OF BISMUTH.—$BiS^3, 3WS^3$.—Dark brown precipitate, which turns black on drying.

BISMUTH AND MOLYBDENUM.

A. MOLYBDATE OF BISMUTH-OXIDE.—Formed by mixing molybdate of potash with nitrate of bismuth-oxide. Lemon-yellow precipitate, soluble in 500 parts of water and in the stronger acids. (Richter.)

B. SULPHOMOLYBDATE OF BISMUTH.—$BiS^3, 3MoS^3$.—Dark brown precipitate. (Berzelius.)

C. PERSULPHOMOLYBDATE OF BISMUTH.—The aqueous solution of persulphomolybdate of potassium gives a red-brown precipitate with bismuth-salts. (Berzelius.)

Bismuth and Chromium.

Chromate of Bismuth-oxide.—Formed by mixing chromate of potash with nitrate of bismuth-oxide.—Lemon-yellow powder, which, according to Moser, is very slightly soluble in water, and, according to Grouvelle, is reddened by potash.—If bichromate of potash be used for the precipitation, the precipitate is likewise pulverulent and lemon-yellow at first, but becomes crystalline and orange-yellow by washing and drying. (Nölle, *Ann. Pharm.* 2, 94.)

Bismuth and Arsenic.

A. Arsenide of Bismuth.—Breithaupt's *Arsenic-glance* from Palmbaum, near Marienberg;—has the aspect of native sulphide of antimony; texture radiated; specific gravity 5·392; not very hard; contains 97 per cent. arsenic and 3 per cent. bismuth. When once set on fire, it continues to burn till it is entirely consumed. (Weissenbach, *J. techn. Chem.* 10, 226; Kersten, *Schw.* 53, 377; *Pogg.* 26, 492.)—*a.* Fourteen parts of bismuth and one part of arsenic yield, when fused together, an alloy which expands strongly in solidifying.—*b.* An alloy of about 3 parts bismuth and 1 arsenic does not expand in solidifying; it has a reddish-white colour, and imperfectly laminar fracture. (Marx, *Schw.* 58, 464.)—*c.* Bismuth, fused with arsenic for a considerable time, retains only $\frac{1}{15}$ of that metal. (Bergman, *Opusc.* 2, 281.)—*d.* The arsenide of bismuth which is precipitated on passing arseniuretted hydrogen gas through bismuth-salts, gives off nearly all its arsenic on distillation. (Berzelius.)

B. Arseniate of Bismuth-oxide.—Precipitated, on adding arsenic acid to a solution of bismuth in nitric acid, in the form of a white, tasteless, difficultly soluble powder (Scheele), which, when ignited with charcoal, is resolved (according to Berzelius) into sublimed arsenic and bismuth containing arsenic, and, according to Thénard, is insoluble in water and in nitric acid, but soluble in hydrochloric acid.

C. Sulpharsenite of Bismuth.—$2BiS^3, 3AsS^3$.—Red-brown precipitate, which turns black on drying, and yields a black-brown powder. Fuses readily, gives off tersulphide of arsenic when more strongly heated, and leaves a fused basic compound not further decomposible by heat. This compound, when solidified, has a steel-grey colour, metallic lustre, and crystalline fracture, and yields a grey powder. (Berzelius.)

D. Sulpharseniate of Bismuth.—$2BiS^3, 3AsS^5$.—Dark-brown, soluble in excess of sulpharseniate of sodium. (Berzelius.)

Bismuth and Antimony.

A. Antimonide of Bismuth.—The two metals unite in all proportions, and form a brittle alloy. The alloy containing equal parts of the two metals expands strongly in solidifying; that which contains 1 part of bismuth with from 2 to 4 parts of antimony, expands less.

B. SULPHANTIMONIATE OF BISMUTH.—Dark-brown precipitate. In consequence of the free acid in the bismuth-solution, this compound cannot be obtained free from uncombined tersulphide of bismuth and pentasulphide of antimony. (Rammelsberg.)

BISMUTH AND TELLURIUM.

A. TELLURIDE OF BISMUTH.—The two metals may be fused together in all proportions. (Berzelius.)

B. SULPHOTELLURIDE OF BISMUTH.—$2BiTe^3, BiS^3$.—*Telluric Bismuth; Spiessglanz-silber* (Werner); *Molybdänsilber* (Mohs); *Prismatoïdal Bismuth-glance* (Wehrle); *Rhombohedral Bismuth-glance* or *Tetradymite* (Hardinger).—Primary form, an acute rhombohedron, *Fig.* 151; also a truncated obtuse rhombohedron, *Fig.* 142. (Breithaupt, *Schw.* 52, 170.) The crystals result from the combination of the faces of two rhombohedrons, more acute than the acute primitive rhombohedron, truncated with *p*-faces. (Haidinger, *Zeitschrift Phys. Math.* 9, 130.) Specific gravity, 7·807...8·44. (Wehrle), 7·514 (Baumgartner). Light lead-grey, inclining to tin-white, with a high lustre. (Wehrle.)

					Berzelius.		Wehrle.
							Schoubkan.
3Bi	639	....	59·66	....	58·30	....	60·0
6Te	384	....	35·86	....	36·05	....	34·6
3S	48	....	4·48	....	4·32	....	4·8
Se		....		....		....	trace
Matrix		....		....	0·75		
$2BiTe^3, BiS^3$	1071		100·00		99·42		99·4

When heated in a glass tube, it yields metallic tellurium which sublimes in drops. Before the blowpipe it fuses readily, exhaling an odour of sulphur and selenium; burns with a bluish flame; forms a yellow film, with white border on the charcoal; and leaves a shining metallic globule, which, on cooling, becomes covered with a reddish film: the reduced metal is brittle, and has a granular fracture. The compound dissolves readily in nitric acid, depositing flakes of sulphur, (Wehrle, *Schw.* 59, 482; *Zeitschr. Phys. Math.* 9, 133 and 144; abstr. *Pogg.* 21, 595 and 599.) The ore from St. Jozé, in Brazil, exhibits similar characters. (Von Kobell, *J. pr. Chem.* 8, 341.)

C. SULPHOTELLURITE OF BISMUTH.—A compound of *Bisulphide of Tellurium* with *Tersulphide of Bismuth.*—Formed by precipitating a bismuth-salt with sulphotellurite of sodium.—Dark-brown precipitate, black when dry; gives off sulphur when distilled, and leaves a grey mass, having the metallic lustre. (Berzelius.)

OTHER COMPOUNDS OF BISMUTH.

With Tin, Lead, Iron, Nickel, Copper, Mercury, Silver, Gold, Platinum, Palladium, and Rhodium, forming easily fusible alloys.

END OF VOL. IV.

LONDON: PRINTED BY HARRISON AND SON, ST. MARTIN'S LANE.

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1850.

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REPORT

OF

THE THIRD ANNIVERSARY MEETING

OF THE

CAVENDISH SOCIETY.

THE Anniversary Meeting of the Cavendish Society for the year 1850 was held at No. 19, Montague Street, Russell Square, on Friday, the 1st of March, at three o'clock in the afternoon.

The Chair was taken by THOMAS GRAHAM, ESQ., F.R.S., PRESIDENT, who called upon the Secretary to read

THE REPORT OF THE COUNCIL.

"The Council have pleasure in announcing to the Members, at this their third Anniversary Meeting, that the Society continues to increase in numbers; and although the extension which it has undergone during the past year has been progressive rather than very considerable, yet it has justified the expectations which were expressed in the last Report, and will enable the Council to fulfil the promises founded thereon.

"Two volumes of the Translation of GMELIN'S 'Handbook of Chemistry' have been supplied to the Subscribers for 1849; and it is intended that the 'Life of Cavendish' shall be issued as a third volume for that year. The Council are glad to find that the former of these works continues to be received with undiminished satisfaction; and they are encouraged by this circumstance in the determination to proceed in its publication with as little delay as possible, although the large amount of matter contained in each of the closely printed volumes renders it more expensive than some of the other works which are in progress.

"A little delay has unavoidably occurred in the completion of the 'Life of Cavendish,' on which Dr. GEORGE WILSON has been for some time engaged; but it is confidently hoped that this work, which is now partly printed, will be very soon ready for circulation; and the Council, whilst regretting their inability to supply it to the Members so soon as was originally specified, have no doubt that the time bestowed upon it will not ultimately be regretted, and that it will prove a valuable addition to Chemical literature.

"Arrangements have been made for the preparation of several works intended for publication during the present and following years.

"The fourth volume of GMELIN'S 'Handbook of Chemistry' is partly printed, and will be ready for distribution in two or three months. The Inorganic part of this work will occupy two volumes, in addition to the above; and it is hoped that the part relating to Organic Chemistry may be commenced in the course of next year.

"Professor EDWARD SOLLY is engaged in making a Translation of the 'Essays of Saussure,' together with an abstract of the works of other contemporaneous writers on the Chemistry of Vegetation, which will probably be completed during this year.

"The Council have also undertaken the publication of a Translation of Dr. LEHMANN'S 'Physiological Chemistry,' the second edition of which has just appeared in German. The increased attention which is now devoted to Animal Chemistry seemed to justify the expectation that a work on this subject would prove acceptable to the Members of the Society, and no modern work of the kind possesses a higher reputation than that of Dr. Lehmann. The Translation will be prepared as expeditiously as possible.

"Allusion was made in the last Report to an abridgement of PERSOZ' work on the 'Art and Theory of Dyeing and Calico Printing,' a Translation of which was intended to be undertaken by the Council; but it has been ascertained, from subsequent inquiry, that the required plates and other illustrations would render such a work too expensive for the present means of the Society, and the further consideration of the subject has therefore been deferred until some more eligible occasion may present itself.

"With reference to the financial statement which accompanies this Report, some explanation is requisite. At the period of the last Anniversary Meeting, the Treasurer had a balance of £220 in his hands, while the liabilities of the Society amounted to about £300. There were subscriptions at that time due, however, which made the income equal to the expenditure for the year. On the present occasion, there is a balance in hand of £278, in addition to which some further subscriptions for 1849 are expected; which amount will barely meet the expenses of the publication of the 'Life of Cavendish' (the third volume for 1849), together with one or two other items, relating to that year, which remain unpaid.

"It is evident, therefore, that with the present number of Members, which does not yet exceed 750, the income of the Society is not sufficient to admit of the yearly publication of three volumes, equal in extent to those hitherto produced. The Council, nevertheless, do not anticipate the necessity for diminishing the amount or value of the annual return made to the Subscribers, but trust that, by directing attention to the subject, the Members throughout the country will be stimulated to increased exertion in extending the limits of the Society, and thus augmenting its available resources.

"The Council cannot conclude this Report without expressing their sense of the obligations due to the Honorary Local Secretaries, whose active exertions on behalf of the Society have so greatly contributed to its success. The subscriptions, *paid in advance*, for each year, being the only means at the command of the Council for meeting the current expenses of publication and management, it is hoped that the Members will co-operate with the Local Secretaries in endeavouring to complete the subscription lists for the several districts at as early a period of the year as possible. If, in addition to increased punctuality in this respect, the number of Members be augmented during this year as much as it was in the last, the Society will be placed in a condition for effectively carrying out its objects to the full extent originally contemplated, and with undoubted advantage to the interests of chemical science."

TREASURER'S STATEMENT of the RECEIPTS and EXPENDITURE of the CAVENDISH SOCIETY, from the 1st of March, 1849, to the 25th of February, 1850.

RECEIPTS.

		£	s.	d.
	Balance from previous year	221	5	2
235	Subscriptions for 1848	247	5	0
673	Ditto 1849	706	13	0
20	Ditto 1850	21	0	0
		£1196	3	2

EXPENDITURE.

	£	s.	d.
Stationery, Postage, Distribution of Books, and Petty cash	23	0	6
Advertisements	15	7	6
Collector's Commission	11	10	10
Editorial expenses	195	15	0
Paper	256	17	11
Printing	286	5	4
Engraver	34	6	9
Binding and wrapping	94	0	10
	917	4	8
Balance in hand	278	18	6
	£1196	3	2

We have examined the above statement, and find it correct.

W. SHARPEY.
W. FERGUSON.
T. N. R. MORSON.

Feb. 25, 1850.

It was moved by Dr. Pitman, seconded by Mr. J. H. Gladstone, and resolved,

"That the Report just read be received and adopted."

The Meeting then proceeded to the election of Officers for the ensuing year—Mr. Samuel Highley, Jun., and Mr. Alfred Smee, having been appointed scrutineers; and the following were declared to have been duly elected:

President.

Professor Graham, F.R.S.

Vice-Presidents.

Arthur Aikin, F.G.S.
Professor Brande, F.R.S.
Earl of Burlington, F.R.S.
Sir James Clark, M.D., F.R.S.
Professor T. Clark, M.D.
Michael Faraday, D.C.L., F.R.S.
Sir R. Kane, M.D., M.R.I.A.
The Marquis of Northampton, F.R.S.
Richard Phillips, F.R.S.
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Jacob Bell, F.C.S.
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Benjamin C. Brodie, F.R.S.
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Henry Beaumont Leeson, M.D., F.R.S., St. Thomas's Hospital.

Secretary.

Theophilus Redwood, Esq., 19, Montague Street, Russell Square.

It was moved by Mr. T. N. R. Morson, seconded by Mr. F. Claudet, Jun., and resolved,

"That Dr. Alfred Taylor, Dr. Semple, and R. Porrett, Esq., be appointed Auditors for the ensuing year."

The following Resolutions were then proposed and unanimously adopted:—

Moved by Mr. AUGUSTUS BIRD, seconded by Mr. HENRY WATTS,

"That the thanks of the Meeting be given to the PRESIDENT, TREASURER, and COUNCIL, for their services to the Society."

Moved by Dr. PEREIRA, seconded by Mr. JACOB BELL,

"That the thanks of the Meeting be given to the HONORARY LOCAL SECRETARIES for their services to the Society."

The Meeting was then adjourned.

THEOPHILUS REDWOOD, SECRETARY,
19, Montague Street, Russell Square.

MARCH 1ST, 1850.

WORKS OF THE CAVENDISH SOCIETY.

1848.

1.—CHEMICAL REPORTS AND MEMOIRS. Edited by THOMAS GRAHAM, F.R.S.

2.—HAND-BOOK OF CHEMISTRY. By LEOPOLD GMELIN. Translated by HENRY WATTS, B.A., F.C.S. Vol. I.

1849.

3.—HAND-BOOK OF CHEMISTRY. By LEOPOLD GMELIN. Vol. II.

4.—DITTO. Vol. III.

5.—THE LIFE AND WORKS OF CAVENDISH, by Dr. GEORGE WILSON, will shortly be ready.

LIST OF MEMBERS.

LONDON.

Aikin, Arthur, F.G.S., 7, Bloomsbury square
Allchin, Alfred, 27, Coles terrace, Barnsbury park, Islington
Anderson, J. B., Great Suffolk street, Southwark
Ansted, D. T., M.A., F.R.S., 36, Gloucester road, Hyde park
Archer, William, London
Ashley, M., College of Chemistry
Atkinson, C., for University College

Baker, Edward, Jun., Bouverie street.
Baker, —, Trinity square, Southwark
Barclay, John, 55, Fore street
Bargent, W. H., 31, Southampton street, Covent garden
Barlow, Rev. J., F.R.S., 5, Berkeley street, Piccadilly
Barnes, Thomas Ilott, Birkbeck Laboratory
Basham, William Richard, M.D., 17, Chester street, Pimlico
Bass, William Thomas, Isendune cottages, Hornsey road
Bastick, W., 2, Brook street, Bond street
Bateman, H., 6, Islington green, Islington
Baylis, John, Ocean's row, Islington
Beaufoy, Henry, South Lambeth
Bell, Jacob, 338, Oxford street
Bellwood, John, 6, Albion place, King's cross
Bird, Golding, M.D., F.R.S., Myddleton square
Bird, Augustus, Hornton villa, Kensington
Blackstone, Samuel H., University College
Blackstone, J., 31, Bayham terrace, Camden town
Blundell, H., 9, Upper Thames street
Bowman, J. E., King's College
Braithwaite, J. C., 17, Bloomsbury square
Brande, William Thomas, F.R.S., Royal Mint
Brodie, Benj. C., F.R.S., 13, Albert road, Regent's park
Brooke, H. J., F.R.S., Clapham Rise
Brown, Thomas, 2, St. Mary-axe
Buchanan, John, Lime street square
Buckton, G. B., 38, Gloucester road, Hyde park
Burlington, Earl of, M.A., F.R.S., 10, Belgrave square
Busk, George, F.R.S., Dreadnought Ship, Greenwich
Butt, Edward, 1 and 2, Kennington road
Button, Charles, 146, Holborn bars

Campbell, Dugald, 7, Quality court, Chancery lane
Cane, R. L., Gutta Percha Company, Wharf road, City road
Carpmael, William, 4, Old square, Lincoln's inn
Catley, —, Jun., 2, Lavender terrace, Wandsworth road
Chabot, P. J., M.A., Fashion street, Spitalfields
Chaplin, John Lambert, 338, Oxford street
Chemical Society, 142, Strand
Chichester, John H. R., 49, Wimpole street
Childs, James, Earls Court, Kensington
Clark, Sir James, Bart., M.D., F.R.S., 22, Brook street
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Coffee, Phillip, Bromley, Middlesex
College of Chemistry (Royal), Oxford st.
College of Surgeons (Royal), Lincoln's Inn fields
College of Civil Engineers, Putney
Compton, Bridmore, 8, Sergeants' Inn
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Cooke, R. H., Abney villas, Stoke Newington
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Cooper, J. T., 82, Great Surrey street
Cowper, Charles, 6, Camden hill villas, Kensington
Cox, Henry, 1, Holford street, Holford square, Pentonville
Craven, Earl of, 16, Charles street, Berkeley square
Crawcour, Isaac Lionel, Guy's Hospital
Cree, David, 42, University street
Curie, P. F., M.D., 17, Hanover square

Dale, Rev. T. P., Amen Court, St. Paul's
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Dalrymple, Grant S., Inst. of Civil Engineers, 25, Great George street, Westminster
Darby, Stephen, 42, Brewer street, Golden square

Deane, Henry, Clapham
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Delarue, Warren, F.R.S., 110, Bunhill row
Delf, Thomas, Bow lane, Cheapside

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Gale, Samuel, 12, Nelson square, Blackfriars
Gann, John William, 171, Fenchurch street
Gassiot, J. P., F.R.S., Clapham common
George, Durancé J., 32, Old Burlington street
Gibbins, H. B., University College
Gibson, J. R., 115, Holborn hill
Gladstone, J. H., Stockwell lodge, Stockwell
Glanfield, George, 17, Bloomsbury square
Glass, William, 7, Ord street, Millwall
Gorr, J., Jun., Brewery, Brick lane, Spitalfields
Graham, Thomas, F.R.S., 4, Gordon square
Greaves, Edmund, 17, Bloomsbury square
Greenhill, J. R., 1 and 2, Kennington road
Griffin, John Joseph, 53, Baker street
Grove, W. R., F.R.S., Siddons' cottage, Upper Baker street
Gutch, J. G., 77, Great Portland street

Hammond, C. W., University college
Hanbury, Daniel, Plough court
Heales, George, Doctors' Commons
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Heisch, Charles, Blackheath
Henderson, William, Copper works, Bow
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Hewitt, Thomas, 9, Terrace, Turnham green
Heywood, J. S. G., Varnish works, Battle bridge
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Hills, Thomas Hyde, 338, Oxford street
Hindsley, Henry, 40, Aldersgate street
Hodgson, C. J., 406, Strand
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Hooper, W., 7, Pall Mall East
Hopkins, W. King, 19, Southampton row
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Ince, Joseph, Southampton street, Covent garden
Inchle, James, 28, Lamb's Conduit street

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Johnson, J. R., 41, Nelson square, Blackfriars
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Joy, F. W., Mr. Deane's, Clapham common
Jukes, J. B., F.G.S., Craig's court

Knight, George, Foster lane, Cheapside

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Leeson, Henry Beaumont, M.D., F.R.S., St. Thomas's Hospital
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Lowe, George, F.R.S., 39, Finsbury Circus
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MacCrea, William, 94, St. John st. road

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Maitland, John, 10, Chester place, Hyde park gardens
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Mathey, George, 79, Hatton garden
Maule, G., 9, Doris street West, Regent street, Lambeth
May, J., Garden wharf, Battersea
Mayall, J. E., 433, West Strand
Maynard, Henry, 17, Park terrace, Highbury
Medico-Chirurgical Society, Royal, Berners street
Miller, W. A., M.D., F.R.S., King's College
Mitchell, John, 23, Hawley road, Kentish Town
Mitchison, F. H., 31, Compton terrace, Islington
Morley, A., Burlington Hotel, Cork street
Morson, T. N. R., 19, Southampton row
Morson, Thomas, Jun., 19, Southampton row
Museum of Practical Geology, Craig's court
Middleton, F., 338, Oxford street

Neale, R., 2, St. George's terrace, Islington
Nesbitt, J. C., Kennington lane
Nicholls, G., University College
Northampton, Marquis of, F.R.S., 145, Piccadilly

Odling, W., 159, High street, Southwark
Okeden, G. F. P., 94, St. John street road
Oldfield, David, Bouverie street

Paris, J. Ayrton, M.D., F.R.S., 27, Dover street
Payne, W., Jun., 6, Church street, Horsleydown
Pepper, J. H., Binfield cottage, Clapham road
Pereira, Jonathan, M.D., F.R.S., 47, Finsbury square
Phillips, Richard, F.R.S., 28, Jermyn st.
Philips, T. T., Grove cottage, Barrington road, East Brixton
Philips, A., 2, Kent Villas, East Greenwich
Pitman, H., M.D., 28, Montague place, Russell square
Playfair, Lyon, F.R.S., 28, Jermyn street
Pollock, Thomas, 129, Fenchurch street
Pontifex, Edmund A., Shoe lane
Porrett, R., F.R.S., 49, Bernard street
Pritchard, Rev. C., Clapham
Prout, W., M.D., F.R.S., 40, Sackville street, Piccadilly

Rains, Alfred, 4, Crescent, New Bridge street
Ramsay, A. C., F.R.S., F.G.S., 27, Edward street, Regent's park
Rea, Edward, Wardour street
Redwood, Theophilus, 19, Montague street, Russell square
Reekes, Trenham, 28, Jermyn street
Reid, Alexander, 5, Bathurst street, Hyde Park gardens
Reynolds, Capt. J. W., 2, Clifton place, Sussex square
Richardson, W., 17, Radnor place, Hyde Park gardens
Richardson, W., 17, St. Helen's place, Bishopsgate
Robson, Joshua, 17, Bloomsbury square
Rogers, Arnold, 16, Hanover square
Roscoe, Henry, 14, Torrington square
Rosling, Alfred, Camberwell terrace
Ross, A., Featherstone buildings, Holborn
Royle, J. F., M.D., F.R.S., Heathfield lodge, Acton
Rudall, F., Jun., University college
Russell, William Jenner, University college
Rust, William, Garden wharf, Battersea

Sainsbury, G., 177, Strand
Saunders, E., 13*a*, George street, Hanover square
Savory, John, 143, Bond street
Scanlan, Maurice, 25, Great George street, Bermondsey
Scott, Lieut., H. R. E., Royal Arsenal, Woolwich
Semple, Dr., 8, Torrington square
Sharpey, Wm., M.D., F.R.S., 35, Gloucester crescent, Gloucester gate, Regent's park
Shearman, Chas. James, B.A., University College Hospital
Simpson, Henry, University College
Simpson, George, 1 Kennington road
Smee, Alfred, F.R.S., 7, Finsbury circus
Smith, George, 29, Finsbury square
Smith, T. B., Copper works, Bow
Smith, —, Tudor house, Camberwell
Smith, John, Jun., Hampstead
Smythe, Warrington, 28, Jermyn street
Solly, Edward, F.R.S., 15, Tavistock square
Southgate, James, 5, Charles street, Middlesex hospital
Spencer, John A., 9, Westbourne place
Squire, Peter, 277, Oxford street
Starkie, Richard, 4, Strand

Steele, R. J., 177, Regent street
Stutfield, W., 139, St. George street, East
Sylvester, John, 96, Great Russell street

Taunton, J. C., 48, Hatton garden
Taylor, A. A., 6, Queen street place, Queen street, Cheapside
Taylor, A. S., M.D., F.R.S., 3, Cambridge place, Regent's park
Taylor, Thomas, Vere street, Cavendish square
Tennant, C., 149, Strand
Terry, William, Peterborough house, Fulham
Teschmacher, E. F., 4, Park terrace, Highbury
Thomas, John J., 94, St. John street road
Thomson, H., University College
Thomson, Thomas, 2, Brunswick place, Regent's park
Tingle, Thomas, Apothecaries' hall, Blackfriars
Tomlinson, C., 12, Bedford place, Hampstead road
Townson, Thomas, Plough court
Tudor, E., Dowgate hill

Vincent, B., for Royal Institution

Wallace, R., 9, John's terrace, Hackney road
Walton, G. H., 43, Lamb's Conduit street
Ward, William, 23, Holles street, Cavendish square
Ward, N. B., Clapham Rise
Warington, Robert, Apothecaries' hall, Blackfriars
Watts, Henry, B.A., University College
Webster, Thos., F.R.S., 2, Great George street, Westminster
Weddell, George, 45, Robert street, Hampstead road
Welch, Ryder, Upper Clapton
Wheatstone, Charles, F.R.S., King's College
White, Alfred, 19, Tyndall place, Islington
White, J. Grove, 18, Wharton street, Pentonville
White, Geo., Currie's Distillery, Bromley
Wildsmith, J. H., Primrose street, Bishopsgate street
Williams, C. J. B., M.D., F.R.S., 7, Holles street, Cavendish square
Williams, John, Jun., Royal Astronomical Society, Somerset house
Williamson, Professor A. W., University College
Wilson, W., 9, Maida hill
Winstanley, E. N., 7, Poultry
Winsor, F., 57, Lincoln's Inn fields
Winston, B., M.D., 59, Gibson square
Woodfall, H. D., Angel court, Skinner st.
Woods, J., 3, Barge yard, Bucklersbury
Wright, F., 7, Bath place, Kensington

Yarde, Giles, 28, Lamb's Conduit street
Yorke, Col. P., F.R.S., 89, Eaton place, Belgrave square
Young, F., 25, Holborn hill

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Bengough, —, Roby place
Blackwell, T., Fox hangers, near Chippenham
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Dutton, T. H. M., 25, Milsom street
Falkener, R. W., Edgar house
Field, F., 2, Northumberland buildings
George, R. F., Royal crescent
Lawson, H.
Morgan, Capt. H. M., Royal crescent
Penny, Thomas, 7, Bridge street
Terry, P., Bailbrook house, Bath Easton
Watts, W. R., Argyle street
Young, —

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Coombs, James
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Adkins, Henry, Summer hill
Birmingham Library, per Mr. Aldri~~tt~~ tn
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Dawes, John, Smethwick
Elkington, George, Northwood
Evans, Brook, Edgbaston
Forbes, David, Espedal, Norway
Gibbs, John
Horncastle, John
Macfarlane, Charles

Mayer, Jos, Longport, Potteries
Palmer, C. F., Colmore row
Parkes, Alexander, Harbourne
Prosser, Richard, 18, Broad street
Ryland, Thomas, Great Lister street
Shaw, George, Queen's College
Ward, N., Chemical works, Oldbury
Wiggin, Henry
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Kempthorne, John

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Bridson, Thomas R., Bridge house
Hardcastle, James, Firwood
Haward, John, Union foundry
Haworth, Thomas, M.D.
Rideout, W. J., Farnworth mills
Rushton, T. L.
Watson, W. B.

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Brighton Literary and Scientific Institution
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Coathupe, Charles Thornton
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Hynes, Mathias
Thomas, Thomas, Jun.

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Brumell, Rev. E., M.A., St. John's Coll.
Fuller, Frederick, Peterhouse
Humphries, G., Caius College
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Blyth, Dr.

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Bury, John, *Hon. Sec.*
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Powell, H., M.D.
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Dawson, —
Derby Mechanics' Institution.
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Hodges & Smith, for Sir Patrick Dun's Library
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Mallett, Robert
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Astley, Thomas
Bain, Alexander
Chalmers, C., Merchiston Castle Bank
Coventry, Andrew, 29, Moray place
How, Henry
Jones, D. F.
Kemp, Alexander T.
Macfarlane, J. F.
Maclagan, D., M.D.
MacLachlan, R.
Macwilliam, W.
Miller, John
Robertson, William, M.D.
Rowney, T. R.
Royal College of Physicians
Royal Edinburgh Medical Society
Taylor, Hugh
Tennant, John
University of Edinburgh

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Ronalds, Edmund, Ph.D., *Hon. Sec.*
Queen's College Library

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Chemical Society of Glasgow, per Dr. R. D. Thomson
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Dunlop, Charles T.
Ferguson, A. A.
Griffin, Charles
Harvey, Alexander
Henry, Alexander
Johnson, James, Greenock
King, James
Macgregor, Robert, M.D.
Napier, John
Napier, Rober
Penny, Dr. F.
Philosophical Society, per A. Liddell
Poynter, John
Ramsay, William
Randolph, C.
Robb, Charles
Stenhouse, John, Ph.D.
Tennant, John
Thomson, F. H., M.D.
Thomson, R. D., M.D.
Walker, Archibald
White, John, Jun.

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Evans, Thomas, M.D.
Gyde, A., Painswick
Hickes, Thomas
Hyett, W. H., Painswick, Stroud
Lovett, John
Rose, J. M.
Tucker, J.

GOSPORT

Allan, James, M.D., *Hon. Sec.*

GUERNSEY.

Hoskins, E., M.D., *Hon. Sec.*
Arnold, Adolphus
Ozanne, John, M.D.

HALIFAX.

Garlick, John W., M.D., *Hon. Sec.*

HELSTON.

Moyle, G. W., *Hon. Sec.*

HEXHAM.

Nicholson, John, *Hon. Sec.*
Donkin, Thomas
Fairless, W. D.
Pearson, William
Pruddah, William

HORSHAM.

Snelling, F., *Hon. Sec*
Poulters, H. I.

HULL.

Pearsall, Thomas, *Hon. Sec.*, 22, John street, Kingston square
Brown, J. Lyne
Cooper, Henry, M.D.
Gleadow, Robert Ward, York parade
Jacobs, Bethel
Richardson, John
Sandall, David
Seaton, J. L.
Sollitt, J. D.
Subscription Library
Thomson, Thomas
Wilkinson, John, Burton-upon-Humber

LEAMINGTON.

Sandall, Samuel Ames, *Hon. Sec.*, Brewery
Busby, Ralph
Doyne, William
Harper, Henry
Middleton, William
Tabberer, William

LEEDS.

Ward, W. Sykes, *Hon. Sec.*, Leathley lodge
Cheetham, Henry, 13, Briggate
Crowther, G. I., Woodhouse
Harvey, Thomas, 13, Briggate
Huggon, William, Photographic Gallery, Park row
Irvine, F. W., M.D., 6, South parade
Joy, Edward, Jun., 25, St. James' street
Macleod, —, M.D., Ilkley
Morley, George, 4, South parade
Nunnelley, Thomas, 7, East parade
Ramsbotham, J. H., Foxly hall, near Huddersfield
Watson, William, jun., Sheepscar
West, W., Highfield house, Dewsbury road
Westley, W. R., 1, Warwick place

LEICESTER.

Stallard, J. H., *Hon. Sec.*, Friar lane
Cooper, —, Market place
Noel, Charles, Pickleton
Plant, James, Sparkenhoe street
Spencer, Thomas, Jun.

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Anderton, Henry, Church road, Much Wootton
Blake, James, 37, Shaw's brow
Clay, Robert, 38, St. Ann street
Clow, John, 54, Mount Pleasant
Cox, James, 13, Catherine street
Crosfield, Simon, 17*a*, Dean st., Fairfield
Dawson, J., Shaw street, Everton
Edwards, J. B., 42, Berry street
Evans, Henry Sugden, 31, Fleet street
Formby, R., M.D., 13, Pilgrim street
Holliday, —
Johnson, William, Birkenhead
Keates, John
Kurtz, A., 63, Kensington
Macculloch, S., 120, Duke street
Macfie, D., 5, Catherine street
Mercer, N.
Muspratt, F., Seaforth hall
O'Dwyer, Thos., M.D., A.B., 31, Hope st.
Rawlins, C. E., Jun., 28, Catherine street
Robinson, M., Warrington
Rowlandson, Thomas
Samuelson, N., 85, Bedford street, South
Waldie, David

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Prothero, D., M.D.
Price, G. P.

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Key, Dr. Thomas

MAIDSTONE.

Walker, David, *Hon. Sec.*

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Antrobus, Thomas, Hyde Print-works, Hyde
Barnes, Joseph, Church, Accrington
Bar, Nathaniel, 52, Burlington street, Manchester
Barnes, John, Church, Accrington
Barnes, Joseph, Jun., Irwell Springs, Bacup
Bates, William, Ardwick green
Becker, E. H., Cross street, Manchester
Beswick, Samuel, 11, George Street
Bevan, James, Bellfield Print-works, Rochdale
Binney, E. W., 40, Cross street
Binyon, Alfred, Mayfield
Binyon, Alfred, Jun., Mayfield
Blake, James, 111, Mount Pleasant, Liverpool
Blythe, William, Holland bank
Brazil, John, Homer terrace, Lower Broughton
Brooks, Thomas, Sunnyside, Rawtenstall
Buckley, William, Horwich, near Bolton
Burd, John, Mount Sion, Radcliffe
Calvert, F. C., Royal Institution
Cameron, James, Cornbrook, Hulme
Campbell, Henry C., Messrs. Paulings, Mosley street
Christie, David, 8, New Cannon street buildings
Clare, Peter, Quay street
Coates, George, Seedly Print-works
Coates, John, Seedly Print-works
Cottam, Samuel E., Brazenose street
Coultate, William Miller, Surgeon, Burnley
Crowther, William, Gomershall, near Leeds
Cunliffe, James, Handforth, Cheshire
Dale, John, Bridge street, Ardwick
Davies, John, Quay street
Dean, James, Dawson croft, Salford

Dickson, Thomas, Mount Sion, Radcliffe
Dugdale, James, Lower house, Burnley
Earle, E., Messrs. Wright & Sons, York st.
Fort, Richard, Read hall, Whalley
Gallemore, John E., Ardwick
Gaskill, Wm. Henry, Manchester
Glover, Walter, Adelphi, Salford
Gatty, A., Church bank, Accrington
Greenwood, John, Irwell Springs, near Bacup
Gorton, Richard, Nicolas street
Gratrix, Wm., Springfield lane, Salford
Grave, John, George street
Halliday, A. P., Cornbrook
Hammond, Peter, Levenshulme
Haworth, Dr. George, Church, Accrington
Heap, R., Cross-hall Print-works, Chorley
Heilman, R., Ardwick Chemical works
Hindle, James, Sabden, near Whalley
Holker, Samuel, Bury
Hoole, William, Blackburn
Horsfall, H. W., Spring Gardens
Heald, Wilson, & Co., Messrs., Strangeways
Hampson, Robert, Clayton bridge, near Manchester
Hargreaves, Brothers, & Co., Messrs., Broad Oake, near Accrington
Heys, P. T., Oxford street
Hutchinson, T. P., Radcliffe
Jackson, Robert, Princess street
Jones, John, Rhodes Print-works, Middleton
Joule, James P., F.R.S., Salford
Kay, Robert, Mosley street
Kenyon, Thomas, Manchester
Kenyon, Henry, West Leigh, Lancashire
Kenyon, Enoch, Strangeways
Kenyon, John, Harpurhey
Knowles, Joshua, 11, George street
Leese, Joseph, Ardwick
Leigh, John, St. John street
Locket, Joseph, Fennel street
Losh, Watson, Charlotte street
McDougal, Alexander, 124, Water street
Macfarlane, William, Burnley Print-works, Burnley
Manchester Royal Infirmary
Margerison, John, Mosley street
Mather, William, Salford
Mather, Colin, Salford
Matley, Richard, 13, High street
Meldrum, Edw., Ardwick Chemical works
Mercer, John, Oakenshaw, near Accrington
Mercer, John, Jun., Oakenshaw, near Accrington
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Mount, John, London road
Mucklow, Edward, Elton Fold, Bury
Neild, Alfred, Mayfield
O'Neill, Charles, Mayfield
Parry, John, Fennel street
Pownall, John, Arlington street, Salford
Price, Thomas, Jun., Bury
Prince, J. D., Lowell, United States
Peel, George, Wakefield
Pochin, H. D., Quay street, Salford
Paton, G., James street, Salford
Pearson, —, Mosley street
Pearson, —, Jun., Mosley street
Ransome, Joseph A., St. Peter's square
Ransome, Thomas, Princess street
Rumney, Robert, Burgesses' terrace, Ardwick
Rooke, Joseph, Union bridge, Red bank
Riley, Whittaker, Castleton Print-works, Rochdale
Schunck, Dr., Bellfield hall, Rochdale
Shaw, Alexander, Stockport
Siemens, C. W., Soho hill, Birmingham
Simpson, James, Foxhill bank, Accrington
Sims, Ollive, Hest bank, Lancaster
Speed, James Wm., Adelphi, Salford
Statham, Jonathan, B., Manchester
Steiner, Frederick, Jun., Accrington
Stephens, Dr. Edward, Bridge street
Stone, Daniel, Devonshire place
Symonds, Stephen, Handforth, Cheshire
Schwabe, Salis, Rhodes Print-works, Middleton
Spence, P., Pendleton Alum-works
Taylor, Richard, Clayton bridge, near Manchester
Thom, John, Mayfield
Thom, David, Whitlane, Pendleton
Thompson, Edmund, Primrose, Clitheroe
Thompson, James, Primrose, Clitheroe
Thompson, James, Ardwick
Thorp, Henry, Mayfield
Utley, Hiram, Surgeon, Burnley
Vernon, John V., Manchester
Walsh, John, Crumpstall bridge
Webb, Thomas George, Glass-works, Ancoats
Weisgerber, James, Foxhill bank, Accrington
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Woodcroft, Rufus, Chapel street, Salford
Woolley, James, Market street
Young, James, Ardwick Chemical-works

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Bell, J. L.
Browell, J. J., Bolden
Glover, R. M., M.D.
Mather, James, South Shields

awson, John
ease, S., North Shields
attinson, H. L.
opwith, Thomas, F.R.S., Allenhead
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rown, James, Ebbw Vale Iron-works, Abergavenny
orthie, J., Newport
Robotham, E., Risca
Rogers, J., Abercarn

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rnold, Edward, *Hon. Sec.*
oileau, Sir J. P., Bart.
am, Frederick, King street
tark, William

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Wright, Thomas, M.D., *Hon. Sec.*, Pelham street
Darby, Augustus, Regent street
Eddison, Booth, High Pavement
Hawksley, Thomas, Trent Water-works
Keely, John, Jun., Castle terrace
Maltby, William, for Medico-Chirurgical Society
Parr, S., Poultry
Smith, Thomas, Stanton hall
White, Joseph, for Library of General Hospital

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Kay, W. J., Royal Marine barracks
Oxland, Robert
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Beatson, William, Rotherham
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Horncastle, H., Far Gate
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Lucas, William, Lead-mills
Manners, Rev. J., Glossop road
Overend, W., Church street
Ray, James, Victoria street
Shearman, C. J., M.D., Rotherham]
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Waddy, Rev. S. D., Wesly College

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Southhouse, Rev. G., Hound
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Tyndale, John

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Dawe, S.
Hermann, B.
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Hill, Benjamin
James, John W.
Jones, W. C.
Llewellyn, Dillwyn
Lowther, Herbert, at French's, Neath
Napier, James
Richardson, Robert
Thomas, James
Wallace, H. R., A.M.
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Lea, John Whaley
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Belcombe, H. S., M.D.
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